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DISSOLVED OXYGEN AND OXIDATION-REDUCTION POTENTIALS IN GROUND WATER

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Water samples were collected from various depths in a pristine sand and gravel water table aquifer at monthly intervals over a period of one year. Dissolved oxygen concentrations were near saturation 9 feet below the water table and decreased to nearly zero at 78 feet below the water table. Changes in the Eh values were consistent with changes in the dissolved oxygen concentrations. Hydrogen peroxide was detected in nanomolar concentrations at all depths, but not on every sampling run. Of all oxidation-reduction potentials calculated from substituting analytical results into the Nernst equation, only the Fe^{3+}/Fe^{2+} couple in the deepest well agreed with the measured Eh within 50 millivolts. For the O_2/H_2O_2 and NO_3^-/NH_4^+ couples the range of potentials calculated from one year's data overlapped the range of measured Eh values, so there was some agreement on the average. However, for a given sampling run, the various calculated potentials spanned several hundred millivolts, which means that the activity ratios for the various couples differed by many orders of magnitude (i.e. the system was not in redox equilibrium). The concentration profiles of many solutes, including dissolved oxygen, suggest mixing of shallow and deep ground waters. The observed concentration profiles were relatively constant over the duration of the sampling.

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FOREWORD

EPA is charged by Congress to protect the Nation's land, air and water systems. Under a mandate of national environmental laws focused on air and water quality, solid waste management and the control of toxic substances, pesticides, noise and radiation, the Agency strives to formulate and implement actions which lead to a compatible balance between human activities and the ability of natural systems to support and nurture life.

The Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the Laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zone of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Currently, there is a very limited amount of information and understanding of oxygen and oxidation-reduction processes in the subsurface environment of ground water. This report is a first attempt at defining and understanding the dynamic relationships involved in this environment. These relationships should be useful to microbiologists, geochemists and engineers studying ground-water quality and the fate of contaminants in ground waters.

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ABSTRACT

Water samples were collected from various depths in a pristine sand and gravel water table aquifer at monthly intervals over a period of one year. Dissolved oxygen concentrations were near saturation 9 feet below the water table and decreased to nearly zero at 78 feet below the water table. Values of Eh reflected the dissolved oxygen concentrations. Hydrogen peroxide was detected in nanomolar concentrations at all depths, but not on every sampling run. Of all oxidation-reduction potentials calculated by substituting analytical results into the Nernst equation, only the Fe^{3+}/Fe^{2+} couple in the deepest well agreed with the measured Eh within 50 millivolts. For the O_2/H_2O_2 and NO_3^-/NH_4^+ couples the range of potentials calculated from one year's data overlapped the range of measured Eh values, so there was some agreement on the average. However, for a given sampling run, the various calculated potentials differed by several hundred millivolts, which means that the activity ratios for the various couples differed by many orders of magnitude (i.e. the system was not in redox equilibrium). The concentration profiles of many solutes, including dissolved oxygen, suggest mixing of shallow and deep ground waters. The observed concentration profiles were relatively constant over the duration of the sampling.

CONTENTS

	Page
Abstract	iv
Acknowledgements	vi
Introduction	1
Conclusions	3
Recommendations	3
Materials and Methods	4
Well Drilling and Installation	4
Water Sampling	5
Analytical Methods	6
Hydrogen Peroxide	7
Results and Discussion	8
Dissolved Oxygen, Trace Metals, and Eh	9
Hydrogen Peroxide	10
Other Solutes	11
Calculating Redox Potentials	13
References	14
Appendices	21
A. Oxygen Diffusion Through Sampling Tubing	22
B. Tabulation of Ground Water Analyses	23
Figures	35

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INTRODUCTION

Because ground water makes up a significant fraction of the water resources of the United States, comprising approximately 40% of the water withdrawn for agricultural, municipal, and industrial use [Anon. 1978], ground-water quality is of great concern. If ground-water quality is defined in terms of the concentrations and properties of substances dissolved in the water, then the presence or absence of dissolved oxygen affects many aspects of ground-water quality. The mobilities, reactivities, and toxicities of many elements may all depend on their oxidation state. Microbial populations are distinctly different in oxic and anoxic waters and, therefore, the rates of microbial degradation of organic compounds are also quite different. Thus, dissolved oxygen affects both the geochemical and microbial processes which are likely to influence water quality. In this project we have begun the chemical characterization of a shallow aquifer with dissolved oxygen concentrations ranging from near-saturation to near-anoxic, conditions that are typical of many aquifers which are susceptible to contamination. The results of this study should, therefore, be useful to microbiologists, geochemists, and engineers studying ground-water quality and the fate of contaminants in ground waters.

Improper disposal of municipal and industrial wastes in landfills and land applications of sludges, industrial wastes, fertilizers, or pesticides can lead to degradation of ground-water quality through leaching of these materials and percolation of the contaminated leachate into shallow aquifers. Aquifer contamination may be partially mitigated by natural physical processes, but the time scale for flushing a conservative substance from an aquifer is proportional to the hydraulic residence time of the ground water, which can be hundreds of years in some aquifers. Furthermore, the time required for the flushing of a hydrophobic contaminant that is strongly sorbed by the aquifer solids may be much longer than the residence time. Clearly, physical processes for aquifer self-purification can be very slow. However, natural chemical and biological processes can also contribute to aquifer self-purification.

The rates of many of these self-purification processes depend on the oxidation-reduction (redox) status of the ground-water/aquifer system. The redox status of the ground water can control the chemical speciation of many elements and can also influence microbial ecology and metabolism. For example, in the pH range of most ground waters, ferric hydroxide is much less soluble than ferrous hydroxide. Also, in oxic systems containing hydrous metal oxides, sorption processes limit the solubilities of many trace elements [Jenne 1968]. For example, arsenate, which is the thermodynamically favored form of arsenic in oxic waters is more strongly adsorbed on metal oxides than arsenite, which is thermodynamically favored in anoxic

waters [Ferguson and Gavis 1972]. Arsenite is, thus, more mobile than arsenate in aquifer systems. Arsenite is also more toxic than arsenate [Lemmo et al. 1983]. Thus, in aquifers in which arsenic-containing minerals are present, redox conditions are very important in determining water quality. In very anoxic waters, precipitation of sulfides controls the solubilities of many elements. The solubilities of such toxic metals as cadmium and lead are likely to be highest in mildly anoxic environments that contain neither sulfide nor metal oxides, which are found in many shallow aquifers.

Redox conditions also influence microbial speciation and metabolic rates. Different classes of bacteria use different elements and compounds as electron acceptors in respiration [Stumm and Morgan 1981, Stanier et al. 1979]. If dissolved oxygen is present in an aquifer, then aerobic organisms predominate. If aerobic respiration depletes the dissolved oxygen in a system that is closed to the atmosphere, such as the deeper parts of an aquifer, then a succession of microbial populations utilizing electron acceptors with decreasing redox potentials may be expected. A typical microbial succession may include aerobes, denitrifiers, fermentors, sulfate reducers, and methanogens. Such microbial successions have been invoked to explain the chemical evolution of ground waters in several aquifers [Champ et al. 1978]. The availability of preferred electron acceptors will affect microbial speciation and the rates of biotransformation of toxic substances. For example, the rate of degradation of DDT is much greater in anoxic freshwater sediment systems than in oxic systems [Gambrell et al. 1984 and references cited therein].

In view of the importance of the redox status of ground water and other natural waters it is desirable to have a convenient, reliable indicator of redox status. The potential of a platinum electrode, or Eh, is often used as a geochemical redox indicator [Garrels and Christ 1965]. This is because the Eh of a water sample can be readily measured and in well defined synthetic solutions the Eh provides a quantitative indicator of redox speciation [Laitinen 1960]. Also, in certain aquatic environments the Eh can be quantitatively related to chemical speciation, e.g. waters of low pH and high Fe concentrations [Nordstrom et al. 1979] and certain anoxic sediments [Emerson 1976]. However, using the Eh as a redox potential for an entire aquatic system is only meaningful in systems that are in chemical equilibrium and that contain electroactive solutes at approximately millimolar concentrations [Stumm and Morgan 1981]. Most ground waters are not in equilibrium [Lindberg and Runnels 1984]. Furthermore, the Eh of natural waters are often mixed potentials determined by two or more redox couples, rather than one dominant couple [Stumm and Morgan 1981]. Thus, it is usually not possible to quantitatively relate chemical speciation and Eh in natural waters.

In spite of its limitations, the Eh can be a useful qualitative indicator of the redox status. Consistently measured or calculated Eh values can indicate relative redox levels in a single system. Such systems may include successive depths in a sediment or zones in flow systems with similar concentrations of major electrolyte ions and electroactive minor ions.

On the other hand, comparison of the Eh values of very different waters, e.g. well-poised anoxic ground waters and poorly-poised oxic ground waters, is probably not meaningful. The most reliable characterization of the redox level of a natural water is a complete chemical analysis, including all redox-active species [Hostetler 1984]. This is the approach which has been taken in this project.

We have been collecting ground water samples from a pristine sand and gravel aquifer in the Sand Ridge State Forest near Havana, Illinois. Using the materials and techniques that are the least likely to disturb the chemistry of the ground waters, we have measured Eh, redox speciation, and complementary chemical parameters that enable calculation of redox conditions in the aquifer. We will report our results and our interpretations, including calculation of redox potentials from analytical data, redox processes causing changes in dissolved oxygen concentrations, the presence of hydrogen peroxide, and physical mixing in the aquifer.

CONCLUSIONS

The relative redox status of ground water at the Sand Ridge site is related to the dissolved oxygen concentration as shown by Eh measurements and chemical speciation calculations. The Eh also qualitatively indicates the relative redox status of the ground waters, i.e. the lower the DO the lower the Eh. In the deepest waters sampled, the Eh is quantitatively related to Fe speciation. However, for other redox couples and at other depths, there is no quantitative relationship between redox speciation and Eh. The aquifer-ground water system is not in redox equilibrium at any depth sampled because calculated redox potentials for several couples differ by up to hundreds of millivolts, corresponding to differences in activity quotients of orders of magnitude. The concentration profile of DO is fairly constant and is consistent with mixing of layers of oxic and anoxic water. Modeling the DO profile may help understand mixing in the aquifer.

RECOMMENDATIONS

The field studies should be expanded to include very anoxic ground waters in a similar hydrologic environment, preferably in the same aquifer. Solid oxidants and reductants in the aquifer can be studied to determine their role in redox processes. Geochemical extractions can give an estimate of the aquifer oxidizing or reducing capacity. Redox titrations of aquifer sediments can estimate the redox buffer capacity of the aquifer system. Respirometry experiments may estimate kinetics of aquifer redox processes. Characterization of the organic matter in ground water is essential to understanding aquifer redox processes in both oxic and anoxic waters. This characterization should include complexation of electroactive metals, which

may influence measured Eh values, and molecular weight and functional group determinations, which can indicate potential substrates for microbial respiration.

MATERIALS AND METHODS

WELL DRILLING AND INSTALLATION

The monitoring wells for ground water sampling were installed in the Sand Ridge State Forest near Havana, Illinois in the Havana Lowlands region. The aquifer being studied is a water table aquifer composed of coarse sand and gravel. The geology and hydrogeology of the area have been described by Walker et al. [1965]. Hydrologic investigations have been conducted in the area by the Illinois State Water Survey [Naymik and Sievers 1983, 1985].

Three wells were drilled in October, 1984 to nominal depths of 35, 50, and 65 feet below grade. One additional well was drilled in September, 1985 to a depth of 104 feet. The wells were drilled with a hollow-stem auger. The auger flights, well casing sections, and well screens were steam cleaned to minimize introduction of foreign matter into the boreholes. During the drilling of the 65-foot and 104-foot wells, split spoon samples of the aquifer material, i.e. coarse sand or sand and gravel, were taken for determination of Fe and Mn oxide contents.

For each well the casing and screen were lowered by hand through the hollow auger stem. When the auger was withdrawn, the sand collapsed around the screen and casing up to the water table, approximately 27 feet below grade. Bentonite pellets were poured into the borehole to form a two-foot barrier to rapid percolation. The hole was then backfilled with drill cuttings to two to three feet below grade. Finally, the hole was filled with expanding cement and a steel locking well protector was inserted and allowed to set in the cement. Details of construction of the wells are shown in Figure 1.

The 50-, 65-, and 104-foot wells were developed by air lifting. An air hose was lowered to the bottom of the well and compressed air was used to force the water out of the well until the expelled water was clear. The water level in the 35-foot well was too low to allow sufficient submergence for development by air lifting. This well was developed by swabbing.

A Teflon positive-displacement bladder pump connected to Teflon tubing was installed in each well. Before installation the pumps and tubing were detergent and acid-cleaned followed by thorough rinsing with deionized water.

WATER SAMPLING

For pH, Eh, specific conductance, and temperature measurements ground water was pumped from the well and through a flow-cell that held the electrodes and probes [Garske and Schock In press]. The cell was designed so that there would be no air contact with the ground water and so that the axes of the pH and Eh electrodes were aligned parallel with, rather than perpendicular to, the direction of flow. This cell design minimizes streaming potential problems in pH and Eh measurements [Gray 1985] as well as preventing accumulation of bubbles in the cell. The pH electrode was calibrated at the temperature of the ground water using two buffers.

The Eh was calculated from redox electrode (Orion 977800) potentials using an empirical equation for reference electrode potential as a function of temperature [Garske, E. E. unpublished data, Illinois State Water Survey, 1984]. The response of the two Eh electrodes was also checked using a redox buffer at the temperature of the ground water. The Eh values calculated using the empirical equation differed from Eh values calculated relative to the buffer by +30 to +80 mV.

Beginning in August, 1985 a polarographic dissolved oxygen (DO) probe (Orion 970800) mounted in a flow-through cell was installed immediately downstream from the flow-cell. The DO probe was calibrated according to the manufacturer's instructions. Conductivity, pH, Eh, and temperature were monitored in the flowing water. When all parameters reached stable values (i.e. less than 0.05 pH units, 10 mV, or 10 $ohms^{-1}$ change in successive casing volumes) the well was considered to be completely flushed. That is, the water that was being pumped from that point on was considered to be representative of the aquifer water. These stable values were recorded.

After well flushing, water samples were collected. Unfiltered water samples were collected for organic carbon, ammonia, hydrogen peroxide, hydrogen sulfide, and dissolved oxygen determinations. Organic carbon samples were collected in precombusted glass vials. Samples for ammonia were preserved with H_2SO_4. Samples for hydrogen sulfide were preserved with zinc acetate and sodium hydroxide. Samples for dissolved oxygen and hydrogen peroxide were analyzed immediately after collection. Oxygen diffusing through the sampling tubing probably did not appreciably contaminate any of our samples from the 35-, 50-, or 65-foot wells, but may have contaminated the samples from the 104-foot well (see Appendix A).

After collection of the unfiltered samples, the sampling tubing was connected to a 90 mm diameter in-line filter holder (Millipore) containing a membrane of nominal pore size 0.1 μm (Nuclepore 141705). (Note: the hose barbs supplied with the filter holder were replaced by pressure-tight tubing fittings.) The in-line filter holder was used to prevent air contact during filtration, which can cause contamination of ground water samples by atmospheric oxygen accompanied by oxidation of ferrous iron [Stolzenberg and Nichols 1985]. Filter membranes of nominal pore size 0.1 μm were used rather than the more commonly used 0.45 μm filters because 0.1 μm filters are more effective for the removal of fine particulate metals from water

samples [Kennedy et al. 1974, Laxen and Chandler 1982]. A new filter membrane was used for each well. At least 500 mL of water was allowed to flow through a new membrane to remove soluble contaminants and to equilibrate the filter surfaces with dissolved trace metals, thus minimizing adsorptive losses [Gardner and Hunt 1981]. After the initial washing, a 500 mL filtered sample was collected for alkalinity determinations. Filtration of the alkalinity sample provided further washing of the filter. Subsequent filtered samples were collected for major cations, anions and silica, and trace metals. Samples for major cations and for trace metals were collected in acid-cleaned bottles and were preserved with 1 percent (by volume) HNO_3 and 0.1 percent HCl, respectively.

Field blanks were collected using the apparatus shown in Figure 2. Deionized water was forced through the filtering apparatus and collected by the same procedure as the water samples. Thus, the field blanks and samples were treated identically.

Water samples were stored on ice immediately after collection. Upon arrival at the laboratory the samples were refrigerated. Nonacidified samples were stored for less than 24 hours before being analyzed.

ANALYTICAL METHODS

Determinations of the unstable solutes dissolved oxygen, alkalinity, and hydrogen peroxide were performed in the field. Dissolved oxygen was determined using the azide modification of the Winkler method [Rand et al. 1975]. Alkalinity was determined by potentiometric titration using Gran's method to locate the equivalence point [Stumm and Morgan 1981].

Manual colorimetric methods were used to determine ammonia [Standard Methods 1975] and iron [Stookey 1970]. Both solutes were below detectable levels in early samples. For the 9/19/85 and 10/17/85 samples from the 104-foot well, Fe and Mn were determined by atomic absorption spectrophotometry. After 12/13/84, samples were screened in the field for NH_3 using a field colorimetric method (Chemetrics, Inc. Calverton, VA). If the NH_3 concentration was less than 0.1 mg L^{-1}, the detection limit of the Chemetrics method, the sample was not analyzed for NH_3.

Automated adaptations of standard colorimetric methods were used to determine orthophosphate, dissolved silica, sulfate, nitrite, and nitrate. Chloride was determined by automated potentiometric titration. Volatile and nonvolatile organic carbon fractions were determined by wet oxidation and infrared CO_2 detection [Barcelona 1984].

Manganese determinations were attempted using two electroanalytical methods. From November, 1984 until March, 1985 cathodic stripping voltammetry [Huber and Lemmert 1966, Hrabankova et al. 1969] using a wax-impregnated graphite electrode. Manganese concentrations in ground water samples were not significantly different from blank Mn concentrations. From 4/23/85 to 6/20/85, anodic stripping voltammetry using a hanging

mercury drop electrode [O'Halloran 1982] was used. However, manganese was not detected in any sample. After the 6/20/85 sampling trip, Mn determinations were discontinued because the concentrations were too low for quantitation.

Hydrogen Peroxide

The fluorimetric scopoletin/horseradish peroxidase method [Andrae 1955] incorporating published modifications [Perschke and Broda 1961, Van Baalen and Marler 1966, Cooper and Zika 1984] and further optimization developed during this project, was used for hydrogen peroxide determinations. The method has been used to measure 2 nM H_2O_2 in rain water [Zika et al. 1982], and recently, H_2O_2 in ground and surface waters [Cooper and Zika 1983]. The method has several advantages over other methods for H_2O_2: 1. It is extremely sensitive, being based on a compound which has detectable fluorescence in concentrations lower than 1 nM; 2. It is rapid, with immediate and complete reaction due to the large turnover rate of the enzyme catalyst; 3. It is selective, since the fluorophore is stable unless oxidized by activated enzyme and the enzyme itself is highly specific for and activated only by peroxides. (The contribution of organic peroxides can be determined separately if necessary.); 4. The stoichiometry has been established--one molecule of fluorophore is oxidized for each molecule of H_2O_2; and 5. It is adaptable to field determinations, eliminating problems of sample instability frequently encountered in determinations of very low levels of H_2O_2.

In the analysis, hydrogen peroxide present in the sample stoichiometrically oxidizes scopoletin, a fluorescent lactone. The reaction is catalyzed by the peroxidase enzyme. The fluorescence of the buffered mixture of sample and reagent is measured before and after the addition of the enzyme, the decrease or quenching of fluorescence being proportional to the amount of hydrogen peroxide present. The fluorescence quenching is related to the concentration of hydrogen peroxide by the method of standard additions. Linear regression on a plot of fluorescence vs. moles added peroxide gives the fluorescence response per mole of hydrogen peroxide reacted. This response factor is used to calculate the amount of hydrogen peroxide in the ground water sample. Ground water samples taken at Sand Ridge were analyzed in triplicate within minutes of collection. At the low observed concentrations, i.e. near the detection limit, it is important to minimize the imprecision of the concentration determinations and the potential for photochemical formation of H_2O_2 in the water sample.

In order to correct for any H_2O_2 contribution from the reagents, we initially analyzed blanks, substituting deionized, distilled, and freshly redistilled water for the sample. However, hydrogen peroxide concentrations in the reagent blanks were equal to or up to three times greater than those of the samples for all sampling runs except 1/17, 3/19, 5/15, and 10/17/85. We suspected that the distilled water contained H_2O_2 and tested this hypothesis by varying the concentrations of scopoletin and peroxidase and by adding the peroxidase before the scopoletin. Varying the reagent concentrations had no effect on the blanks and the H_2O_2 signal in the blanks was

eliminated by addition of the enzyme prior to the scopoletin. Therefore, the measured quenching in the reagent blanks was due to H_2O_2 present in the distilled water.

Hydrogen peroxide contamination of distilled water may be the major problem with obtaining reliable reagent blanks. The stoichiometry of the reaction in distilled water blanks has been found to be 0.7 to 0.9 moles of scopoletin per mole of hydrogen peroxide, which is close to the accepted value of 1.0 [Perschke and Broda 1961]. This supports the hypothesis of H_2O_2 contamination of the distilled water and suggests that side reactions are not responsible for quenching.

Blanks have not been addressed in the literature on this method. However, a number of authors have suggested that H_2O_2 can be produced in deionized distilled water as a result of microbial activity [Lazrus et al. 1985], photochemical reactions [Zika 1984], or by sparging with air [Zika et al. 1982]. Perschke and Broda [1961] suggested successive distillation of blank and reagent water from $KMnO_4$, $AgNO_3$, and finally from a quartz still to achieve sufficient water purity. However, none of the previous workers reported any problems with background H_2O_2 concentrations in their experiments.

We have further investigated the origin of the H_2O_2 contamination in the distilled water. We did not observe increases in the levels of H_2O_2 in the water during storage over those in freshly distilled water. Also, sparging the water with oxygen-free nitrogen for several hours did not reduce the levels of H_2O_2 either. The most likely source of the H_2O_2 contaminant is in the distillation process or is carried over from the original amount in the deionized water.

Only one set of measurements of H_2O_2 in distilled water using the scopoletin/peroxidase method has been reported [Perschke and Broda 1961]. In this paper the water was redistilled from $KMnO_4$, $AgNO_3$, and finally, from a quartz still. Unfortunately, since the experiments were intended only to establish the stoichiometry of the reaction, the background contribution of H_2O_2 in the distilled water was not reported. It is likely that hydrogen peroxide is a normal trace component of our distilled water, produced from the water itself and varying with inputs of radiation and dissolved oxygen. Therefore, while a large fraction of our H_2O_2 determinations do not satisfy the conventional analytical criterion of low blanks, we feel that we have positively identified H_2O_2 in ground waters from the Sand Ridge site.

RESULTS AND DISCUSSION

The results of chemical analyses of ground water samples from the monitoring wells in the Sand Ridge State Forest are presented in Appendix B. Aqueous ammonia, sulfate, phosphate, and dissolved silica concentrations are expressed as milligrams of solute per liter (mg L^{-1}). For example, a

sulfate concentration of 1 mg L^{-1} is equivalent to 0.0104 millimolar (mM). For nitrate and nitrite the concentrations are expressed as mg N per liter, i.e. a concentration of 1 mg NO_3^- per liter is equivalent to 0.0714 mM. Alkalinities are in units of milliequivalents per liter (meq L^{-1}) and can be converted to milligrams per liter as $CaCO_3$ by multiplying by 50.

DISSOLVED OXYGEN, TRACE METALS AND EH

The dissolved oxygen (DO) profile for 9/19/85 is shown in Figure 3. The profile of the upper three wells was typical of all sampling runs. The 35-foot sample had the highest DO concentration, which was near the DO saturation limit at the ground-water temperature. The 50-foot sample was near DO saturation with about 1 mg L^{-1} less than in the 35-foot sample. The 65-foot sample had less than 4.5 mg L^{-1} DO. The DO measured in the deepest sample was approximately 0.2 mg L^{-1}. However, because of the presence of Fe^{2+} and Mn^{2+} in the deep waters, (described below) the measured DO was probably an artifact of sampling. The suspected DO contamination may have resulted from gas diffusion through the sampling tubing (Appendix A). Thus, 0.2 mg L^{-1} may actually be an upper limit to the DO concentration in the deep ground waters. The gradient in DO may be caused by mixing of recharge water saturated in DO with deep ground water that is anoxic and contains solutes, such as Fe^{2+}, that consume DO. The time series graph of DO (Figure 4) shows fluctuations of up to 1.5 mg L^{-1} in one month at all depths. This is greater than the uncertainty of +/- 0.2 mg L^{-1} in the Winkler DO determinations, so the observed fluctuations were not an artifact of the analyses. There were no temporal trends in DO at any depth.

The Eh in the aquifer is related to the DO as shown by comparing the profiles of DO and Eh (Figures 3 and 5, respectively). The Eh values are high in oxic waters from shallow and intermediate depths and low in the nearly anoxic deep waters. The relative values of Eh measured in the 35-, 50-, and 65-foot wells were typical of all sampling trips with the highest Eh measured in the waters from 35 feet, the lowest Eh in the 65-foot waters, and a range of less than 50 mV. The time series graph of Eh values (Figure 6) shows that, with the exception of 2/19, 3/19, and 9/19/95 the Eh in the three shallow wells varied between +330 and +430 mV. The spread in Eh values for the 35-, 50-, and 65-foot wells was nearly constant for all sampling trips and agreement between duplicate readings was usually good.

Iron and Mn concentrations were below the detection limits of the ferrozine colorimetric and differential pulse anodic stripping voltammetric methods, approximately 2 and 1 µg L^{-1}, respectively, in all samples from the 35-, 50-, and 65-foot wells. In the samples from the 104-foot well, Fe and Mn concentrations were approximately 0.5 and 0.2 mg L^{-1}, respectively. Assuming that most of the dissolved Fe is ferrous, the partial pressure of oxygen in equilibrium with this Fe^{2+} concentration at the pH of the 104-foot well is approximately 10^{-57} atmospheres, more than 50 orders of magnitude less than the partial pressure calculated from the measured DO concentration. Using the rate law for the oxidation of ferrous iron by dissolved oxygen [Stumm and Lee 1961, Singer and Stumm 1970, Morgan and Stumm 1964],

the half-life of ferrous iron in the aquifer should be less than two hours, which is certainly much shorter than the hydraulic residence time. These discrepancies were probably the result of oxygen contamination during sampling.

HYDROGEN PEROXIDE

The time series graph of hydrogen peroxide is shown in Figure 7. The highest concentrations were measured on 1/17/85. The 2/19/85 concentrations were somewhat lower than those observed on 1/17. There was no consistent profile for H_2O_2.

Hydrogen peroxide is an important intermediate in the reduction of oxygen in natural waters, a reaction which may be written as the product of two two-electron reductions as shown in equations 2-5 [Breck 1974]

$$O_2 + 2\ H^+ + 2\ e^- \Longrightarrow H_2O_2 \quad (2)$$
$$H_2O_2 = H^+ + HO_2^- \quad (3)$$
$$H_2O_2 + 2\ H^+ + 2\ e^- \Longrightarrow 2\ H_2O \quad (4)$$
$$HO_2^- + H_2O + 2\ e^- \Longrightarrow 3\ OH^- \quad (5)$$

where arrows indicate reactions proceeding in one direction and an equals sign indicates equilibrium. A steady state concentration may develop as the result of balancing production and consumption reactions.

The O_2/H_2O_2 couple may be a significant participant in the redox chemistry of certain natural waters, but its influence has not been studied. In principle, the oxidizing power of dissolved oxygen can be controlled by the kinetics of its reduction; if the rate of reduction of H_2O_2 is slower than the rate of its formation, then the potential is effectively that of reaction 4 and O_2 becomes a weaker oxidant than if it were directly reduced to H_2O [Stumm and Morgan 1981]. The reactivity of H_2O_2 is limited by the stability of the O-O bond, which has half the strength of a single covalent bond. Although the disproportionation of H_2O_2 to H_2O and O_2 is favored thermodynamically (delta G = -234 KJ $mole^{-1}$), it is kinetically slow in the absence of trace metal or enzyme catalysts [Hoffmann 1984]. Thus, the low Fe and Mn concentrations in the oxic shallow ground waters at Sand Ridge may contribute to the persistence of H_2O_2.

The contribution of the O_2/H_2O_2 couple to the redox potential measured in natural waters may be important [Breck 1974], but has not been assessed. In the Sand Ridge ground waters, H_2O_2 concentrations may be comparable to those of other electroactive solutes. For example, dissolved Fe concentrations were below the detection limit of approximately 2 $\mu g\ L^{-1}$, or 36 nM, which is similar to H_2O_2 concentrations measured on some sampling trips.

There is now evidence that H_2O_2 is formed, and accumulates, in the photooxidation of organic compounds in surface and ground waters [Cooper and

Zika 1983]. However, the presence of H_2O_2 in untreated ground water has not previously been reported. The superoxide radical anion has been implicated as a precursor of H_2O_2 [Cooper and Zika 1983]. It may be formed by many reaction pathways in natural waters, including the reduction of dissolved oxygen by trace metals [Zika 1984]. Hydrogen peroxide is formed microbially as a by-product of the destruction of the toxic superoxide radical anion [Stanier et al. 1979]. Hydrogen peroxide might accumulate in water due to its slow kinetics of decomposition or the presence of tolerant organisms lacking peroxidase or catalase enzymes for its destruction. For example, bottom waters of the Volga River contain hydrogen peroxide concentrations 1.5 to 2 times higher than in surface waters, due to biochemical processes [Sinel'nikov and Liberman 1974]. Since H_2O_2 concentrations in precipitation are frequently orders of magnitude greater than in ground water [Zika et al. 1982] due to atmospheric photoproduction, rain water may also be a source of peroxide in ground water (i.e. relict H_2O_2 from recharge).

Van Baalen and Marler [1966] first measured H_2O_2 in unfiltered sea water, suggesting that it might be a "significant ecological variable". Concentrations from 15 to 200 nanomolar were found in the surface ocean. From samples taken at several sites they concluded that H_2O_2 was a ubiquitous solute in sea water in the sampling area. No evidence was available as to the source of the oxidant, but atmospheric photoproduction and precipitation, photocatalysis by pigments in the open water, and microbial activity were suggested. Kok [1980] measured H_2O_2 in rain water, finding 5 to 47 micromolar H_2O_2 and a dependence of the concentration on "photochemical activity prior to the rainfall". Zika et al. [1982] found variations in rain water from south Florida and Bahama Islands from 14 to 75 micromolar. Draper and Crosby [1983] reported levels from less than the minimum detectable for their assay, 2 μM, to 30 μM in irradiated, highly eutrophic surface waters. The photoproduction of H_2O_2 from naturally occurring organics, including humic compounds, was observed. Cooper and Zika [1983] exposed unfiltered surface water and ground water to sunlight and determined that H_2O_2 photoproduction was a function of the total organic carbon content of the water, specifically the concentration of humics. Measurements of H_2O_2 in eight ground waters prior to sunlight irradiation were below unreported minimum detectable concentrations. They were probably less than 5 nM [Zika et al. 1985]. The identification of superoxide as the H_2O_2 precursor suggested to the authors that other transient reactive species, such as hydroxyl radical and "organic radicals and metastable intermediates of many transition metals and nonmetallic elements" might be involved in the redox chemistry of natural waters. It was concluded that the levels of H_2O_2 measured in irradiated waters could affect the poise, or redox buffering intensity, of the systems. Studies of H_2O_2 photoproduction in several ground waters and surface waters indicated that there was little production of H_2O_2 in waters with low UV absorbances at wavelengths above 250 nm, corresponding to low concentrations of humic substances [Cooper and Zika 1984]. Despite the wide-ranging sampling and detailed analysis of H_2O_2 photoaccumulation rates, the only measurements of H_2O_2 in ground waters prior to irradiation were below detection limits [Cooper and Zika 1983].

OTHER SOLUTES

The concentration profiles of Ca, Mg, alkalinity, and specific conductance (Figure 8) show a sharp decrease between 35 feet and 50 feet with a smaller decrease between 50 and 65 feet. These profiles were consistent for all sampling runs. There was a small decrease between 65 and 104 feet in alkalinities and concentrations of Ca and Mg. The specific conductance profile is consistent with the profiles of the major ions. The time series graphs of Ca, Mg and alkalinity are shown in Figures 9-11. Alkalinities and Ca, and Mg concentrations tend to increase with time at depths of 35 and 65 feet and are fairly constant at 50 feet. There are concentration fluctuations of more than 0.5 mg L^{-1} $month^{-1}$ at all depths.

The concentration profiles of Na, K, sulfate and chloride (Figure 12) for were typical of all observed profiles. There was a decrease between 35 and 50 feet for all four solutes. Between 50 and 65 feet concentrations of Na, K, and chloride concentrations changed by small amounts, either increasing or decreasing, while sulfate increased. Between 65 and 104 feet Na and K increased slightly while chloride and sulfate changed very little. Sodium and sulfate concentrations increased with time in the 35-foot samples, similarly to Ca, Mg, and alkalinity, while K and chloride showed no trend with time (Figures 13-16).

The pH profile (Figure 17) was typical of all sampling runs with pH increasing from 35 to 65 feet. There was a decrease in pH from 65 to 104 feet. The pH of 35-, 50-, and 65-foot ground waters passed through a maximum on 12/13/84 and varied only within 0.3 units for the rest of the sampling runs.

The concentration profiles of nitrate and orthophosphate (Figure 18) were representative of most sampling runs. Nitrate concentrations decreased with depth, while phosphate concentrations increased. The decrease to a nearly undetectable nitrate concentration in the 104-foot well is consistent with the sharp decrease in DO and Eh between 65 and 104 feet. However, reduced nitrogen species, nitrite or ammonia, were not detected. Nitrate concentrations tended to decrease with time (Figure 19), while phosphate concentrations showed no particular trend after a sharp drop between 11/13/85 and 12/13/85 (Figure 20).

The concentration profiles of DO, NO_3^-, and , possibly, $o\text{-}PO_4^{3-}$ for 9/19/85 have two inflection points. All three profiles are concave upward from 35 to 65 feet and concave downward from 50 to 104 feet. Concentrations of NO_3^- and DO decrease with depth, while $o\text{-}PO_4^{3-}$ concentrations increase with depth. Concentration profiles like these can be produced by diffusion/dispersion. The conceptual model is that upgradient from the monitoring wells two layers of ground water with different concentrations of DO and nitrate are separated by a thin transitional region. Diffusion and dispersion causes the transitional layer to broaden and produces the observed profile. The analogous heat transfer problem, which is mathematically identical, is that of two semi-infinite rods of the same material but at different temperatures that are placed face to face.

Solutions to this problem have been published [e.g. Churchill 1941]. It may be possible to estimate the average dispersion coefficient in the aquifer by modeling the concentration profiles of DO, nitrate, and other solutes.

The time series graph of total organic carbon (TOC) in the 35-, 50-, and 65-foot monitoring wells is shown in Figure 21. There are considerable changes in TOC with time at all depths. Some of the TOC changes in consecutive months were in the same direction, i.e. in one month the changes at 35, 50, and 65 feet were all increases or all decreases. In other months the changes at different depths were in different directions. There did not appear to be a consistent profile of TOC. Wood and Peraitis [1984] observed that DO decreased and the partial pressure of CO_2 increased with depth below the active soil zone, probably due to microbial respiration. We compared month-to-month changes in DO and TOC in an attempt to explain the observed variations in DO, with significant correlation indicating control of DO by microbial respiration. However, the relative uncertainty in TOC measurements was too large to make meaningful correlations.

CALCULATING REDOX POTENTIALS FROM ANALYTICAL DATA

At equilibrium the potential of a redox couple is given by the Nernst equation (equation 6)

$$E = E^{o} + (RT \ln 10 / nF) \log(Ox/Red) \qquad (6)$$

where E is the potential, E^{o} is the standard potential (a constant), R is the gas constant, T is absolute temperature, n is the number of electrons transferred, F is Faraday's constant, and Ox and Red are the product of chemical activities of the oxidized and reduced sides of the stoichiometric equation, respectively. At 12°C, the temperature of Sand Ridge ground waters, the value of $RT\ln 10/F$ is 56.6 mV. In a solution containing more than one redox couple at equilibrium, all potentials calculated by equation 6 are equal. However, natural waters are rarely in redox equilibrium [Stumm and Morgan 1981]. Thus, the potentials calculated using equation 11 for a natural water are strictly theoretical. In this section we describe how potentials are calculated from analytical data and compare measured and calculated potentials.

The redox couples considered were O_2/H_2O_2, Fe(III)/Fe(II), NO_3^-/NH_4^+, Mn(III)/Mn(II) and SO_4^{2-}/HS^-. For each couple a range of potentials was calculated based on ground water analyses in Tables 1-12 and these calculated potentials are compared to the observed range of Eh values.

The potential of the O_2/H_2O_2 couple is given by equation 7

$$E(mV) = 695 + 28.3 \left(\log(DO/54.1) - 2\,pH - \log[H_2O_2] \right) \qquad (7)$$

where the standard potential at 12°C is 695 mV, square brackets indicate molar concentrations, DO is dissolved oxygen in mg L^{-1} and 54.1 is the factor that converts DO to oxygen partial pressure at 12°C. (Strictly speaking, activities should be used in the Nernst equation, rather than concentrations. However, O_2 and H_2O_2 are uncharged species, so their activity coefficients were assumed to be 1.0. Because pH measures H+ activity, no further ionic strength correction is necessary.) The maximum calculated O_2/H_2O_2 potential was for water samples collected from the 35-foot well with a DO of 9 mg L^{-1}, and pH of 7.5. The minimum potential was for 65-foot samples with DO of 3 mg L^{-1} and pH of 8. The DO concentrations measured in the 104-foot well were not considered because it was felt that the values were questionable. A range of H_2O_2 concentrations of 0.1-10.0 nM was assumed for these calculations. The DO-H_2O_2 potentials ranged from +430 to +525 mV, which overlaps the observed range of most of the Eh measurements for the 35- to 65-foot ground waters, roughly +350 to +450 mV.

For the NO_3^-/NH_4^+ couple only nitrate was detected. As a result, the Nernst equation becomes an inequality (equation 8)

$$E(mV) > 884 + 7.08 \left(\log[NO_3^-] - 10\ pH - \log DL \right) \qquad (8)$$

where the standard potential at 12°C is 884 mV and DL is the detection limit for ammonia nitrogen (0.05 mg L^{-1}). (Because the activity coefficient for singly charged ions at the ionic strength of Sand Ridge ground waters was 0.92 as calculated by the Davies approximation, the concentration of nitrate was used in place of the activity.) The minimum nitrate concentration in ground waters from 35 to 65 feet was 21 micromolar in a 65-foot sample. The calculated lower bound for NO_3^--NH_4^+ potentials was +324 mV, which is consistent with the observed range of Eh values. If the NH_4^+ concentration were less than 7 ng L^{-1}, then the calculated potentials would fall in the observed Eh range. The NO_3^--NH_4^+ potential for the 104-foot ground waters of +333 mV is far from the observed value of +110 mV.

Iron and manganese were below detection in all samples collected from the 35-, 50-, and 65-foot wells. However, hydrous oxides of Fe and Mn were found in aquifer sand samples. Thus, lower bounds for apparent potentials of couples involving these metals can be calculated assuming equilibrium with the oxides. For the couple $Fe(OH)^3/Fe^{2+}$ the Nernst equation becomes the inequality given by equation 9

$$E(mV) > 756 + 56.6 \left(\log K - 3\ pH - \log DL \right) \qquad (9)$$

where a detection limit of 1 µg L^{-1} is assumed for Fe determination by the ferrozine method, all soluble Fe is assumed to be Fe^{2+}, and K is the equilibrium constant for dissolution of $Fe(OH)_3$. The value of K at 12°C is 4.88

[Langmuir 1969]. (Note that the only variable in equation 9 is pH.) The lower bound for the $Fe(OH)_3/Fe^{2+}$ potential was estimated to be +155 mV, which is not close to the observed Eh values, but is at least consistent. If the Fe^{2+} concentrations were less than 20 ng L^{-1}, and Fe^{3+} levels were in equilibrium with $Fe(OH)_3$ as assumed, then the calculated $Fe(OH)_3$-Fe^{2+} potential would fall in the observed Eh range.

Iron was detected in the 104-foot ground waters. It was assumed that all soluble Fe was in the ferrous form. The activity of Fe^{2+} was calculated assuming equilibrium with sulfate and hydroxide complexes and using the extended Debye-Huckel approximation to calculate the activity coefficient. The activity of Fe^{2+} was substituted for the detection limit in equation 9. The calculated $Fe(OH)_3/Fe^{2+}$ potential was +38 mV. An uncertainty in the value of the solubility product of $Fe(OH)_3$ of one logarithmic unit, a pH reading that was high by 0.33 pH units, or a combination of smaller uncertainties in these parameters would explain the disagreement between the calculated and measured potentials. The solubility product determined at 25°C was used for the potential calculation because the enthalpy change of the reaction was not listed, which precluded a temperature correction. Thus, the calculated $Fe(OH)_3/Fe^{2+}$ potential agrees reasonably well with Eh. FeOOH was also considered as the phase controlling Fe^{3+}. Because the value of log K for FeOOH is 0.98, the calculated potentials were lower than those calculated assuming $Fe(OH)_3$ control by approximately 200 mV. This disagreement cannot be rationalized in terms of experimental uncertainties. Obviously, it is important to know the form of hydrous Fe oxide present in the aquifer.

Manganite, MnOOH, was assumed to be the form of hydrous Mn oxide present in the aquifer. For $MnOOH/Mn^{2+}$ in the 35- to 65-foot ground waters bounds for calculated potentials were derived similarly to those above for Fe (equation 10).

$$E\ (mV) > 1491 + 56.6\ (\ -\log DL - 3\ pH\ ) \qquad (10)$$

As with the Fe calculations the only variable in this inequality is pH. The lower bound for Mn potentials calculated according to equation 5 is +570 mV, which is greater than all but two extreme Eh values. In order for the calculated Mn potential to fall in the measured Eh range the Mn^{2+} concentration would have to be greater than 40 mg L^{-1}, which would have been easily detectable. The standard potential for MnO_2/Mn^{2+} is higher than that for $MnOOH/Mn^{2+}$, so the potentials calculated for the former couple disagreed with measured potentials by an even greater amount. Manganese was detected in the 104-foot waters. However, assuming the presence of MnOOH at 104 feet, the calculated Mn potential is +474 mV, which is much higher than the observed value of +100 mV. Apparently the $MnOOH$-Mn^{2+} couple is not at equilibrium in the aquifer.

Measured and calculated potentials are compared in Figure 22. The best agreement between calculated and measured potentials was for Fe in the nearly anoxic 104-foot well. The potentials of the other couples differed

from Eh by amounts that were not possible to explain by experimental uncertainty. In the shallower, oxic wells, the range of potentials calculated for the O_2-H_2O_2 couple overlapped the range of Eh values measured over one year. However, for individual samples, the differences between calculated and measured potentials correspond to differences in the ratio of O_2 to H_2O_2 concentrations of many orders of magnitude. Similar lack of agreement between measured potentials and potentials calculated from analytical data has been noted by Lindberg and Runnels [1984], in their examination of published ground water data. In certain special situations measured Eh values have been found to correspond to speciation of one or more elements. These environments include waters of streams receiving acid mine drainage and having low pH values and high Fe concentrations [Nordstrom et al. 1979], anoxic ground waters having high Fe concentrations [Back and Barnes 1965], and anoxic sediment interstitial waters having high sulfide concentrations [Emerson 1976]. However, in oxic waters at near neutral pH the measured Eh is usually far from that calculated from elemental speciation. The probable reason for the lack of agreement between measured and calculated Eh is that the system is not in chemical equilibrium.

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APPENDIX A

OXYGEN DIFFUSION THROUGH SAMPLING TUBING

Oxygen is known to diffuse through polymeric materials, including Teflon. (Teflon membranes are used in polarographic oxygen analyzers [Hitchman 1978].) Thus, it is possible that our ground water samples were contaminated by atmospheric oxygen. If this were true, then our dissolved oxygen measurements would be biased and there could have been some oxidation of ferrous iron before sample acidification. To estimate the extent of this contamination we assumed that the gradient of oxygen fugacity across the tubing wall is linear and equal to the difference between the fugacity inside and outside the tube divided by the tubing thickness. Assuming steady state in a completely mixed control volume of tubing and rearranging terms yields equation A1

$$d\, f(O_2) / dx = (2 \pi r K \Delta f) / (Q \Delta r) \qquad (A1)$$

where $f(O_2)$ is the oxygen fugacity, r is the distance from the center of the tube, $\Delta f / \Delta r$ is the gradient of O_2 fugacity, Q is the flow rate, and K is the mass transfer coefficient for O_2 through Teflon. The dimensions of K are (cm^3 O_2 at STP) (cm^{-2} sec^{-1}) (cm of Teflon) (cm of Hg)$^{-1}$ and the magnitude is approximately 1×10^{-9} [Personal communication, William Buxton, Du Pont Company, February 1985]. Integration of equation B1 gives

$$z / z_o = \exp(-2 K L / (K_H Q)) \qquad (A2)$$

where z is the difference in O_2 fugacity (in atmospheres) between the atmosphere and the inside of the tube at a given point, L is the distance from the beginning of the tube to the point of integration, and Z_o is the value of z at the beginning of the tube, i.e. at L = 0. The difference in fugacity is defined by equation A3

$$z = 0.2 - DO / K_H \qquad (A3)$$

where the approximate fugacity of O_2 in air is 0.2 atmospheres, and K_H is the Henry's law constant for oxygen dissolution. For initially anoxic water being pumped through 100 feet of tubing at a rate of 1000 mL min^{-1} the measured DO would be 0.14 mg L^{-1}, which is similar to the observed DO values. For waters having initial DO values of 3.5 and 8.5 mg L^{-1}, the calculated increases in DO would be 0.10 and 0.03 mg L^{-1}, respectively. These increases are less than the uncertainty in the Winkler titration.

Using the rate law for ferrous iron oxidation by dissolved oxygen [Stumm and Morgan 1981] it is possible to predict the rate of oxidation due to O_2 diffusion through sampling tubing. The resulting system of differential equations cannot be conveniently solved in closed form. We used a fourth-order Runge-Kutta method [Kreyszig 1972] to solve the equations numerically. The solutions for a number of initial conditions (DO, Fe^{2+}) and pumping rates are presented in Table A1. The flow rates of 100 and 1000 mL min^{-1} are typical of flow rates during ground water filtration and sampling for DO measurements, respectively. The DO concentrations of 0, 3.5, and 8.5 mg L^{-1} are typical of ground waters from 104, 65, and 35 feet depths, respectively. If this model is correct, then oxygen contamination can seriously affect the determination of DO, Fe speciation, and, possibly, Eh in mildly anoxic ground waters. We are planning experiments to test the diffusion hypothesis.

TABLE A1. OXYGEN DIFFUSION THROUGH SAMPLING TUBING

Initial DO Concentration (mg L^{-1})	Initial Fe^{2+} Concentration (μM)	Flow Rate (ml min^{-1})	DO Increase (ml min^{-1})	Fe^{2+} Decrease (μM)
0.0	0.00	100	1.36	--
0.0	1.00	100	1.36	0.85
0.0	0.00	1000	0.14	--
0.0	1.00	1000	0.14	0.99
3.5	0.00	100	0 .94	--
3.5	0.00	1000	0.10	--
8.5	0.00	100	0.33	--
8.5	0.00	1000	0.03	--

APPENDIX B

TABULATION OF GROUND WATER ANALYSES

TABLE B1. ANALYSES OF GROUND WATER SAMPLES COLLECTED 11/13/84

Depth (feet)	35	50	65
Temperature (degrees C)	13.2	13.1	12.0
pH	7.90	8.09	8.19
Eh1[a] (mv)	379	374	374
Eh2[a] (mv)	379	357	374
Conductivity (µS/cm)	310	255	208
Alkalinity (meq/L)[b]	3.69	3.20	2.45
Ammonia	<0.05	<0.05	<0.05
Nitrite	<0.01	<0.01	<0.01
Nitrate	1.72	1.46	2.03
Sulfate	32.9	19.7	19.1
Chloride	2.38	1.88	1.96
Orthophosphate	0.14	0.16	0.17
Sulfide	<0.025	<0.025	<0.025
Dissolved Silica	14.4	14.4	13.3
Purgeable Organic Carbon	1.6	1.7	1.4
Nonpurgeable Organic Carbon	0.7	0.4	0.4
Calcium	55.7	45.5	36.7
Magnesium	19.4	16.5	13.4
Sodium	2.66	2.23	1.97
Potassium	0.59	0.57	0.47
Iron (µg/L)	<0.1	<0.1	<0.1
Manganese (µg/L)	<0.05	<0.05	<0.05

Notes: [a]E1, E2 are Eh values calculated according to equation 1.
[b]Concentration units are mg/L except as noted.

TABLE B2. ANALYSES OF GROUND WATER SAMPLES COLLECTED 12/13/84

Depth (feet)	35	50	65
Temperature (degrees C)	11.1	10.3	9.7
pH	8.20	8.46	8.66
Eh1 (mv)	338	341	338
Eh2 (mv)	336	339	335
Conductivity (µS/cm)	272	235	180
Alkalinity (meq/L)	3.81	3.42	2.45
Ammonia-N	0.140	0.098	0.071
Nitrite	<0.01	<0.01	<0.01
Nitrate	1.20	1.42	1.56
Sulfate	34.8	19.7	19.7
Chloride	1.95	1.33	1.60
Orthophosphate	<0.050	<0.050	0.055
Total Phosphate	<0.050	<0.050	0.067
Dissolved Silica	15.2	15.1	13.9
Nonpurgeable Organic Carbon	0.7	0.7	0.7
Purgeable Organic Carbon	2.0	1.6	2.2
Calcium	56.0	47.6	36.0
Magnesium	19.6	17.2	12.8
Sodium	2.8	2.4	2.0
Potassium	0.8	0.8	0.4
Iron (µg/l)	<2.0	<2.0	<2.0
Manganese (µg/l)	<1.0	<1.0	<1.0
Dissolved Oxygen	9.30	8.00	4.21
Hydrogen Peroxide (nM)	6.9	2.8	6.5

TABLE B3. ANALYSES OF GROUND WATER SAMPLES COLLECTED 1/17/85

Depth (feet)[a]	35	65
Temperature (degrees C)	8.9	8.6
pH	7.73	8.17
Eh1[b] (mv)	293	264
Conductivity (µS/cm)	224	165
Alkalinity (meq/L)	3.79	2.38
Ammonia-N	<0.05	<0.05
Nitrate	1.16	1.28
Sulfate	30.34	20.13
Chloride	2.09	1.56
Orthophosphate	<0.05	<0.05
Dissolved Silica	15.2	13.8
Nonpurgeable Organic Carbon	0.5	0.7
Purgeable Organic Carbon	1.7	1.6
Calcium	56.4	36.2
Magnesium	19.6	12.8
Sodium	2.8	2.0
Potassium	0.8	0.4
Iron (µg/l)	<2.0	<2.0
Manganese (µg/l)	<1.0	<1.0
Dissolved Oxygen	10.8	4.1
Hydrogen Peroxide (nM)	62.0	38.0

Notes: [a]Water froze in 50-foot well tubing.
[b]One redox electrode not working.

TABLE B4. ANALYSES OF GROUND WATER SAMPLES COLLECTED 2/19/85

Depth (feet)	35	50	65
Temperature (degrees C)	10.5	10.2	10.4
pH	7.65	7.96	8.16
Eh1 (mV)	532	539	517
Eh2 (mV)	553	562	538
Specific conductance (µS/cm	320	250	210
Alkalinity (meq/L)	4.43	3.64	2.77
Nitrate	1.58	1.43	1.17
Sulfate	35.7	17.9	22.7
Chloride	2.70	2.17	5.70
Dissolved Silica	15.5	15.1	14.2
Prugeable organic carbon	3.9	1.1	0.9
Nonpurgeable organic carbon	3.8	1.3	1.1
Calcium	58.0	44.8	36.4
Magnesium	20.2	16.7	13.6
Sodium	2.8	2.0	2.0
Potassium	0.8	0.4	0.4
Iron (µg/L)	<2.0	<2.0	<2.0
Dissolved Oxygen	10.2	9.4	5.3
Hydrogen Peroxide (nM)	23.0	2.9	7.5

TABLE B5. ANALYSES OF GROUND WATER SAMPLES COLLECTED 3/19/85

Depth (feet)	35	50	65
Temperature (degrees C)	13.0	14.5	13.2
pH	7.57	7.82	8.01
Eh1 (mV)	386	386	372
Eh2 (mV)	408	407	388
Conductivity (µS/cm)	358	270	224
Alkalinity (meq/L)	4.10	3.02	2.42
Ammonia	<0.05	<0.05	<0.05
Nitrate	0.84	1.04	1.60
Sulfate	42.1	18.5	22.3
Chloride	2.28	0.68	1.10
Orthophosphate	0.0173	0.0300	0.0668
Dissolved Silica	16.3	15.7	14.5
Purgeable Organic Carbon	0.6	0.4	0.5
Nonpurgeable Organic Carbon	1.2	<0.1	0.1
Calcium	58.3	43.4	36.4
Magnesium	21.1	16.5	13.8
Sodium	2.6	2.0	1.9
Potassium	0.7	0.6	0.6
Iron (µg/l)	<2.0	<2.0	<2.0
Manganese (µg/l)	<1.0	<1.0	<1.0
Dissolved Oxygen	9.6	8.6	3.7
Hydrogen Peroxide (nM)	<1.0	1.3	4.2

TABLE B6. ANALYSES OF GROUND WATERS SAMPLES COLLECTED 4/23/85

Depth (feet)	35	50	65
Temperature (degrees C)	13.0	13.2	13.1
pH	7.55	7.71	7.97
Eh1 (mV)	321	321	314
Eh2 (mV)	359	359	342
Conductivity (µS/cm)	340	265	225
Alkalinity (meq/L)	3.86	3.07	2.46
Nitrate	1.26	1.07	0.89
Sulfate	40.0	20.0	20.0
Chloride	2.33	1.26	1.50
Orthophosphate	0.023	0.035	0.072
Dissolved Silica	15.2	13.8	15.0
Purgeable Organic Carbon	<0.1	<0.1	0.2
Nonpurgeable Organic Carbon	0.2	<0.1	0.4
Calcium	60.2	44.7	37.2
Magnesium	20.4	16.0	13.4
Sodium	2.76	2.08	1.91
Potassium	0.66	0.62	0.54
Iron (µg/l)	<2.0	<2.0	<2.0
Dissolved Oxygen	9.8	8.6	4.5
Hydrogen Peroxide (nM)	<1.0	1.3	<1.0

TABLE B7. ANALYSES OF GROUND WATER SAMPLES COLLECTED 5/15/85

Depth (feet)	35	50	65
Temperature (degrees C)	12.6	13.0	13.1
pH	7.47	7.76	7.95
Eh1 (mV)	424	412	407
Eh2 (mV)	443	431	427
Conductivity (µS/cm)	350	270	230
Alkalinity (meq/L)	3.95	3.13	2.53
Nitrate	1.43	1.09	0.77
Sulfate	41.4	19.2	23.3
Chloride	1.95	0.82	1.02
Orthophosphate	<0.010	<0.010	0.053
Dissolved Silica	15.1	14.9	14.0
Purgeable Organic Carbon	0.2	0.4	0.2
Nonpurgeable Organic Carbon	0.9	0.6	0.4
Calcium	60.2	44.3	37.2
Magnesium	20.4	15.9	13.2
Sodium	2.74	2.10	1.93
Potassium	0.64	0.60	0.52
Dissolved Oxygen	9.5	8.8	4.2
Hydrogen Peroxide (nM)	8.5	2.3	1.9

TABLE B8. ANALYSES OF GROUND WATER SAMPLES COLLECTED 6/20/85

Depth (feet)	35	50	65
Temperature (degrees C)	11.9	12.7	13.0
pH	7.40	7.67	7.90
Eh1 (mV)	429	423	348
Eh2 (mV)	411	409	361
Conductivity (µS/cm)	149	120	70
Alkalinity (meq/L)	4.18	3.19	2.66
Nitrate	1.44	1.22	0.45
Sulfate	46.0	21.7	27.6
Chloride	2.36	1.25	1.41
Orthophosphate	0.018	0.046	0.088
Dissolved Silica	15.1	14.9	14.0
Purgeable Organic Carbon	1.7	0.2	0.1
Nonpurgeable Organic Carbon	<0.1	0.1	<0.1
Calcium	61.8	45.2	38.9
Magnesium	21.6	16.7	14.2
Sodium	2.88	2.19	2.05
Potassium	0.65	0.61	0.54
Dissolved Oxygen	9.4	7.9	4.5

Note: Hydrogen peroxide analyses not performed.

TABLE B9. ANALYSES OF GROUND WATER SAMPLES COLLECTED 7/23/85

Depth (feet)	35	50	65
Temperature (degrees C)	11.2	11.9	12.2
pH	7.56	7.83	8.04
Eh1 (mv)	385	379	371
Eh2 (mv)	375	367	357
Conductivity (µS/cm)	355	258	237
Alkalinity (meq/L)	3.69	2.97	2.59
Nitrate	1.18	0.97	0.56
Sulfate	42.3	23.7	31.6
Chloride	2.44	2.18	1.41
Orthophosphate	0.019	0.037	0.028
Dissolved Silica	15.7	15.2	14.2
Purgeable Organic Carbon	<0.1	<0.1	<0.1
Nonpurgeable Organic Carbon	0.8	<0.1	0.4
Calcium	65.0	43.7	39.9
Magnesium	22.4	16.1	14.6
Sodium	2.96	2.14	2.10
Potassium	0.66	0.60	0.56
Dissolved Oxygen	10.3	9.4	4.5
Hydrogen Peroxide (nM)	<1.0	5.8	<1.0

TABLE B10. ANALYSES OF GROUND WATER SAMPLES COLLECTED 8/22/85

Depth (feet)	35	50	65
Temperature (degrees C)	11.9	12.8	13.4
pH	7.57	7.76	8.13
Eh1 (mV)	433	421	381
Eh2 (mV)	435	420	376
Conductivity (µS/cm)	317	228	228
Alkalinity (meq/L)	4.37	3.13	2.74
Nitrate	1.07	0.89	0.43
Sulfate	44.5	20.5	28.6
Chloride	2.34	1.15	1.49
Orthophosphate	0.0100	0.0167	0.0670
Dissolved Silica	15.0	14.5	13.9
Purgeable Organic Carbon	0.7	0.6	0.7
Nonpurgeable Organic Carbon	0.7	<0.1	0.3
Calcium	63.2	42.5	41.0
Magnesium	22.6	16.2	15.4
Sodium	2.80	2.00	2.00
Potassium	0.60	0.50	0.50
Dissolved Oxygen	9.4	8.0	4.2

Note: Hydrogen peroxide analyses not performed.

TABLE B11. ANALYSES OF GROUND WATER SAMPLES COLLECTED 9/19/85

Depth (feet)	35	50	65	104
Temperature (degrees C)	12.5	13.4	13.8	15.9
pH	7.60	7.91	8.08	7.77
Eh1 (mV)	568	557	524	114
Eh2 (mV)	555	546	504	116
Conductivity (µS/cm)	325	234	230	223
Alkalinity (meq/L)	4.16	2.98	2.73	2.39
Nitrate	1.06	0.80	0.34	0.04
Sulfate	43.8	19.9	29.4	28.6
Chloride	2.45	1.14	1.42	1.30
Orthophosphate	0.004	0.021	0.051	0.101
Dissolved Silica	15.7	15.1	14.3	16.4
Nonpurgeable Organic Carbon	0.7	0.2	0.1	0.4
Calcium	65.6	42.3	41.9	38.6
Magnesium	22.7	16.0	15.6	12.3
Sodium	3.00	2.04	2.13	3.06
Potassium	0.66	0.58	0.54	0.72
Iron	<0.08	<0.08	<0.08	0.49
Manganese	<0.03	<0.03	<0.03	0.18
Dissolved Oxygen	8.5	7.3	3.5	0.2
Hydrogen Peroxide (nM)	4.5	1.7	1.7	2.3

TABLE B12. ANALYSES OF GROUND WATER SAMPLES COLLECTED 10/17/85

Depth (feet)	35	50	65	104
Temperature (degrees C)	12.0	11.8	12.1	12.4
pH	7.76	8.04	8.21	8.00
Eh1 (mv)	418	420	401	109
Eh2 (mv)	394	396	381	101
Conductivity (mS/cm)	345	235	236	230
Alkalinity (meq/L)	4.52	3.00	2.86	2.59
Nitrate	0.86	0.77	0.42	0.03
Sulfate	46.0	20.9	29.6	27.8
Chloride	2.58	1.18	1.50	1.46
Orthophosphate	0.04	0.04	0.07	0.11
Dissolved Silica	15.4	14.6	14.0	15.8
Calcium	68.2	42.8	43.2	39.0
Magnesium	23.9	16.1	16.1	12.5
Sodium	3.08	2.03	2.14	3.03
Potassium	0.68	0.58	0.56	0.72
Iron	<0.08	<0.08	<0.08	0.46
Manganese	<0.03	<0.03	<0.03	0.16
Dissolved Oxygen	9.7	8.5	3.1	0.7
Hydrogen Peroxide (nM)	27.5	[a]	22.0	[a]

Note: [a]Hydrogen peroxide only determined in 35- and 65-foot samples.

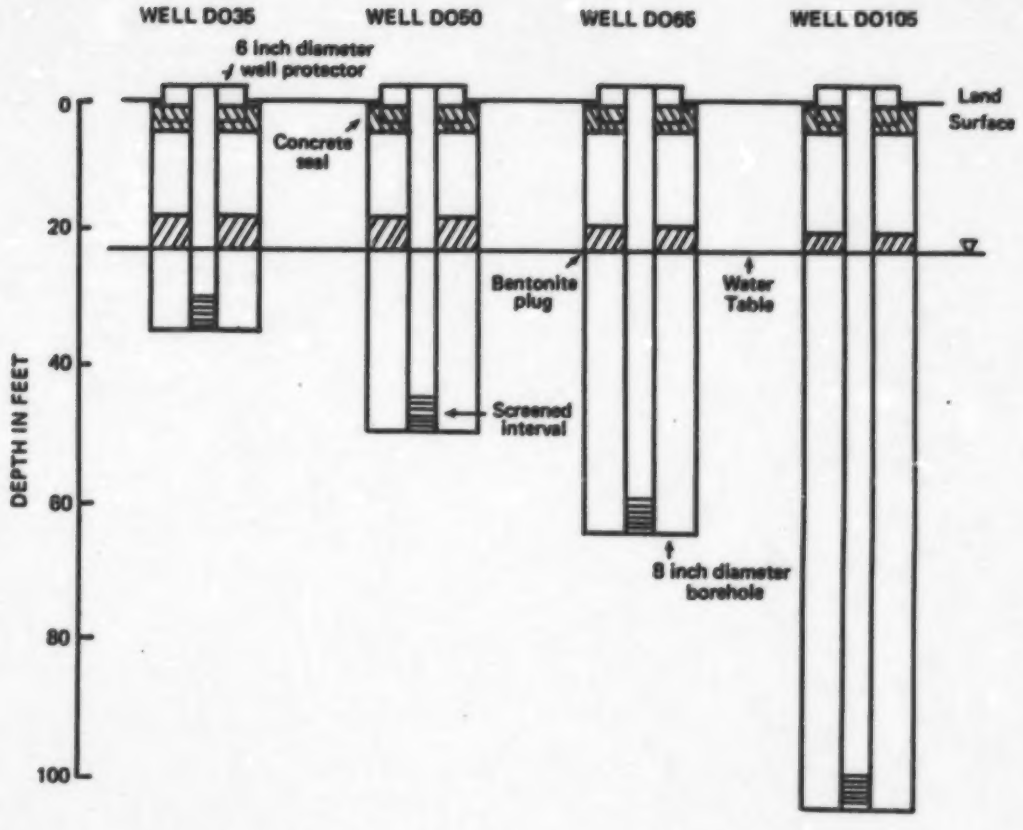

Figure 1. Construction of monitoring wells.

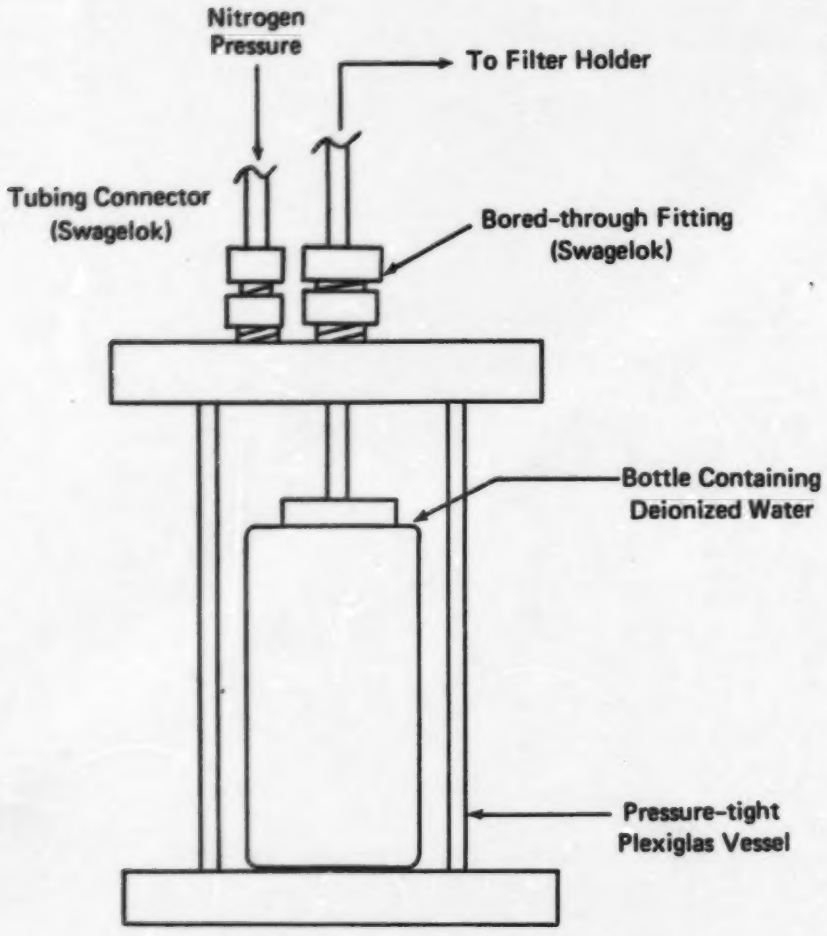

Figure 2. Apparatus for filter blanks.

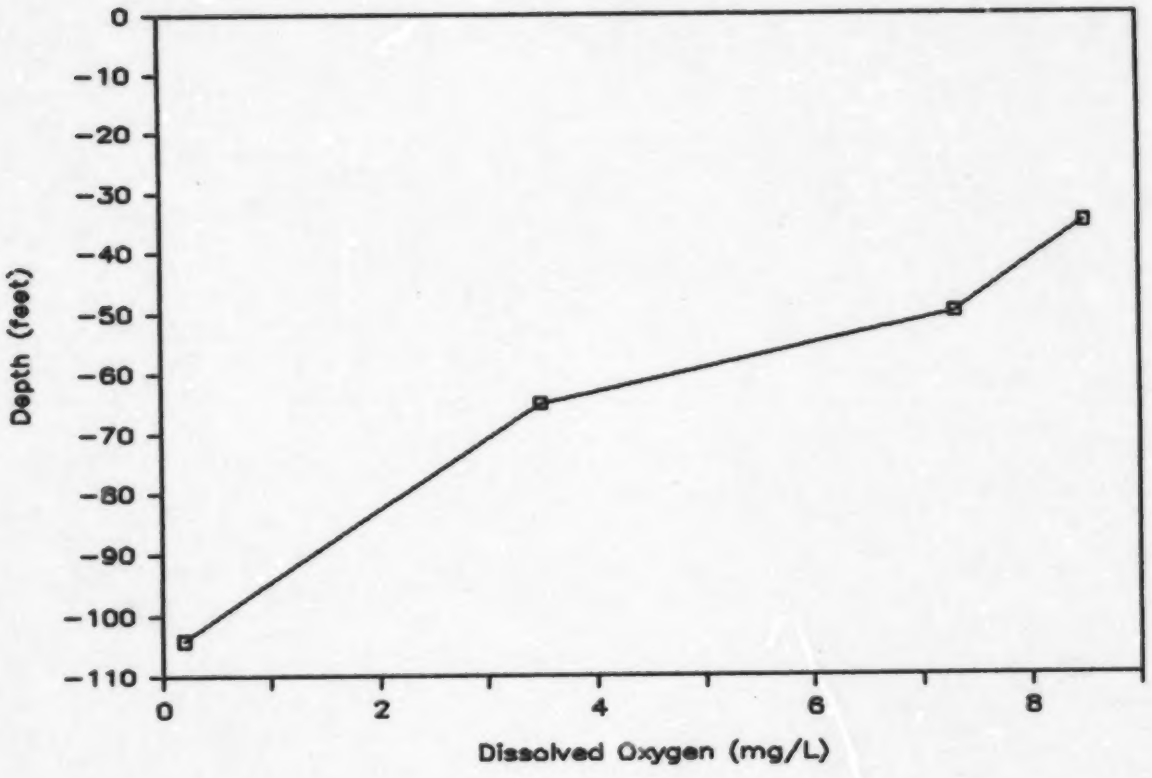

Figure 3. Concentration profile of dissolved oxygen in Havana lowlands aquifer, 9/19/85.

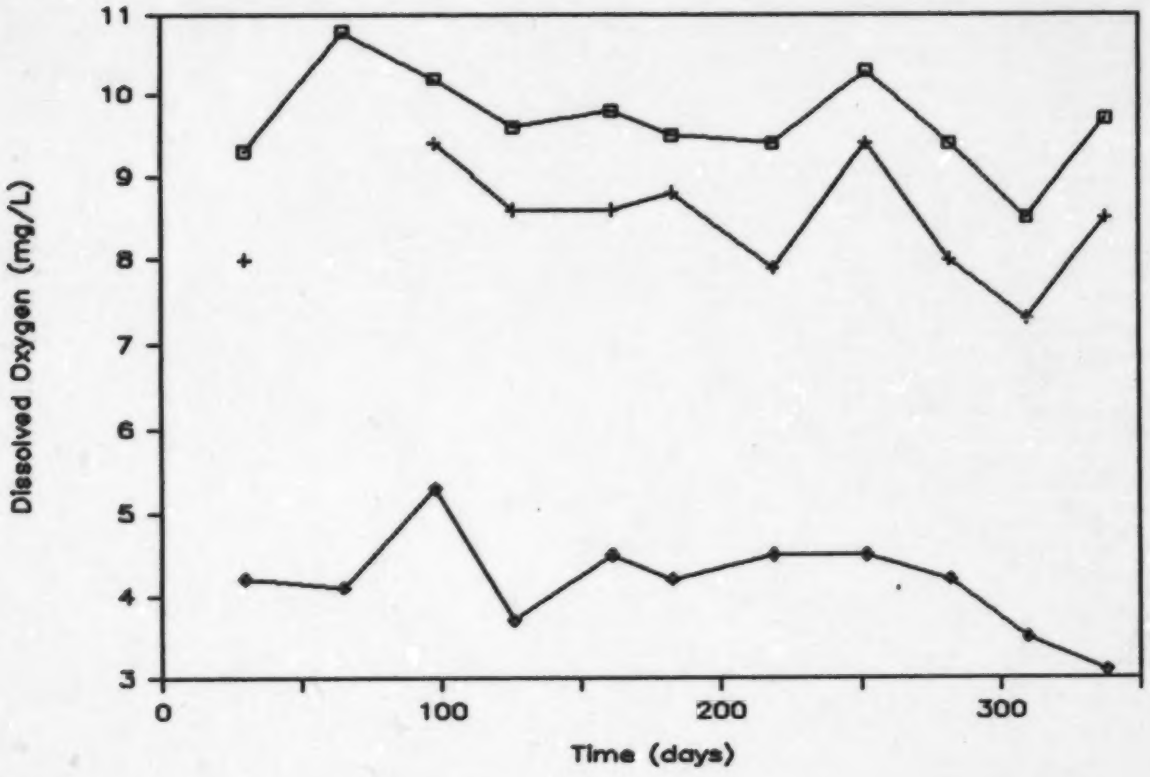

Figure 4. Time series graph of dissolved oxygen concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

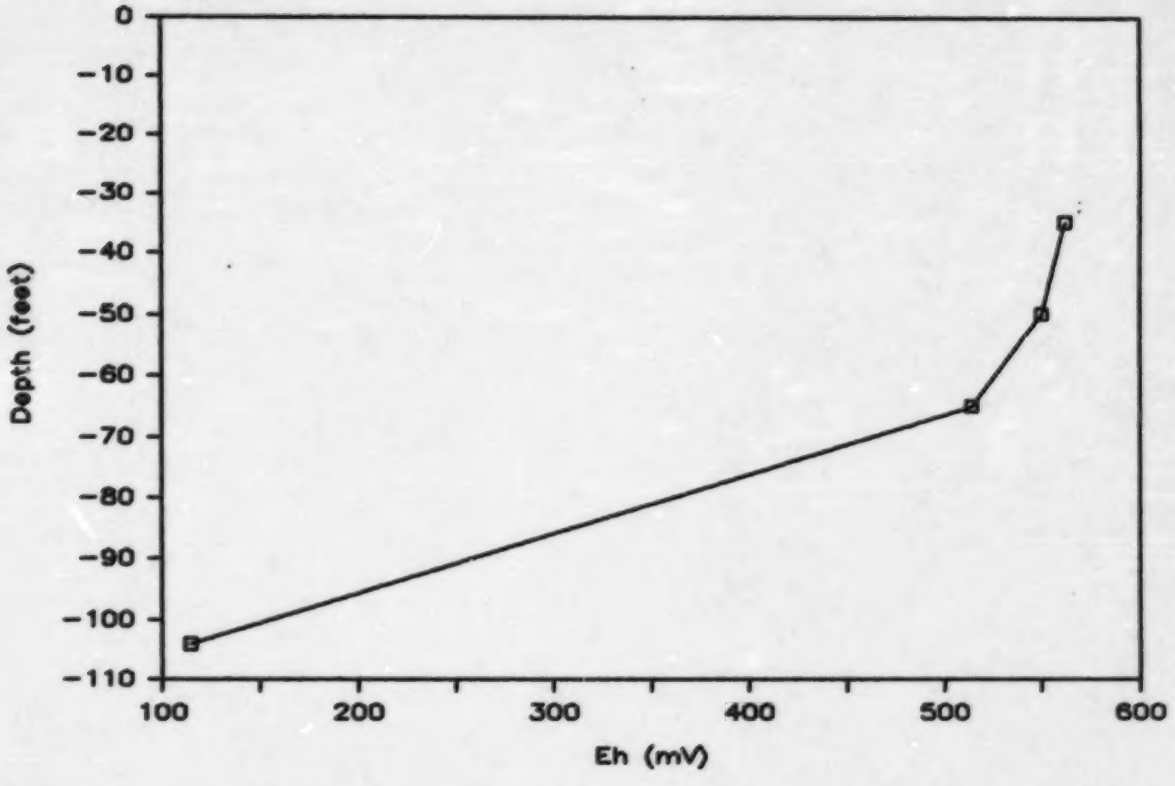

Figure 5. Profile of Eh values in Havana lowlands aquifer, 9/19/85.

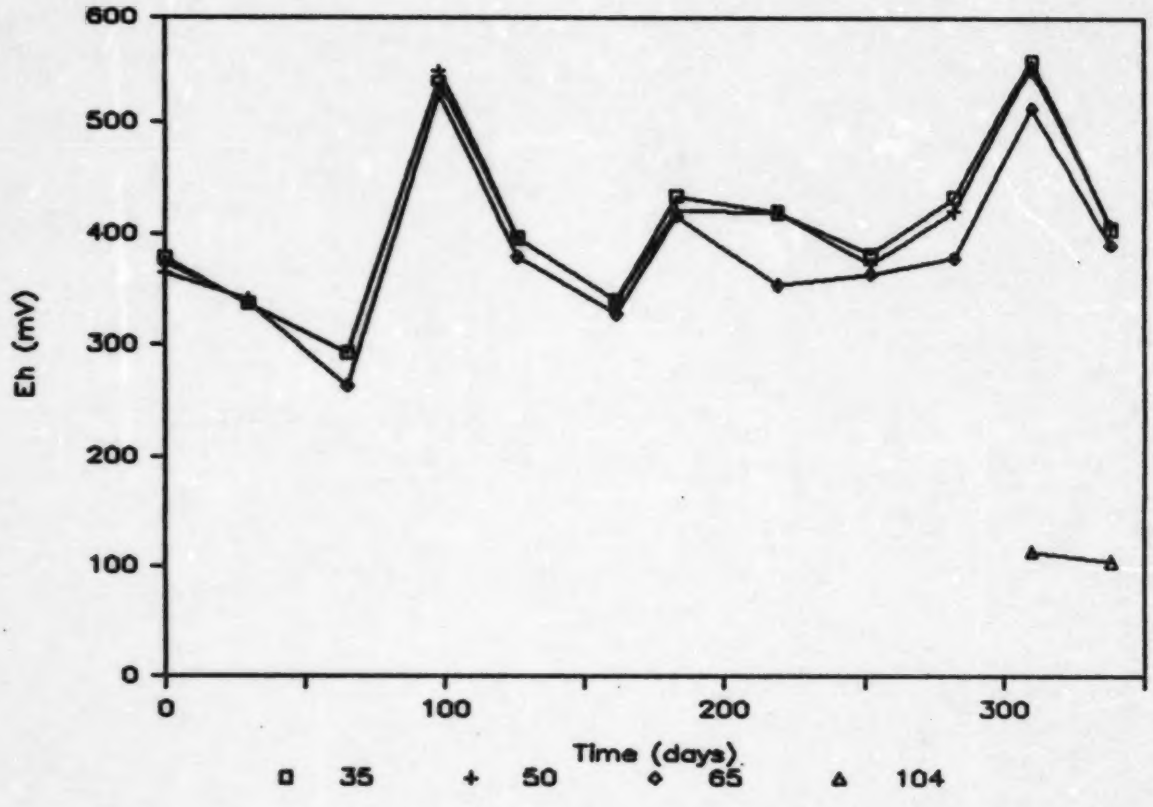

Figure 6. Time series graph of Eh values in Havana lowlands aquifer. □ 35, + 50, ◇ 65, △ 104 feet.

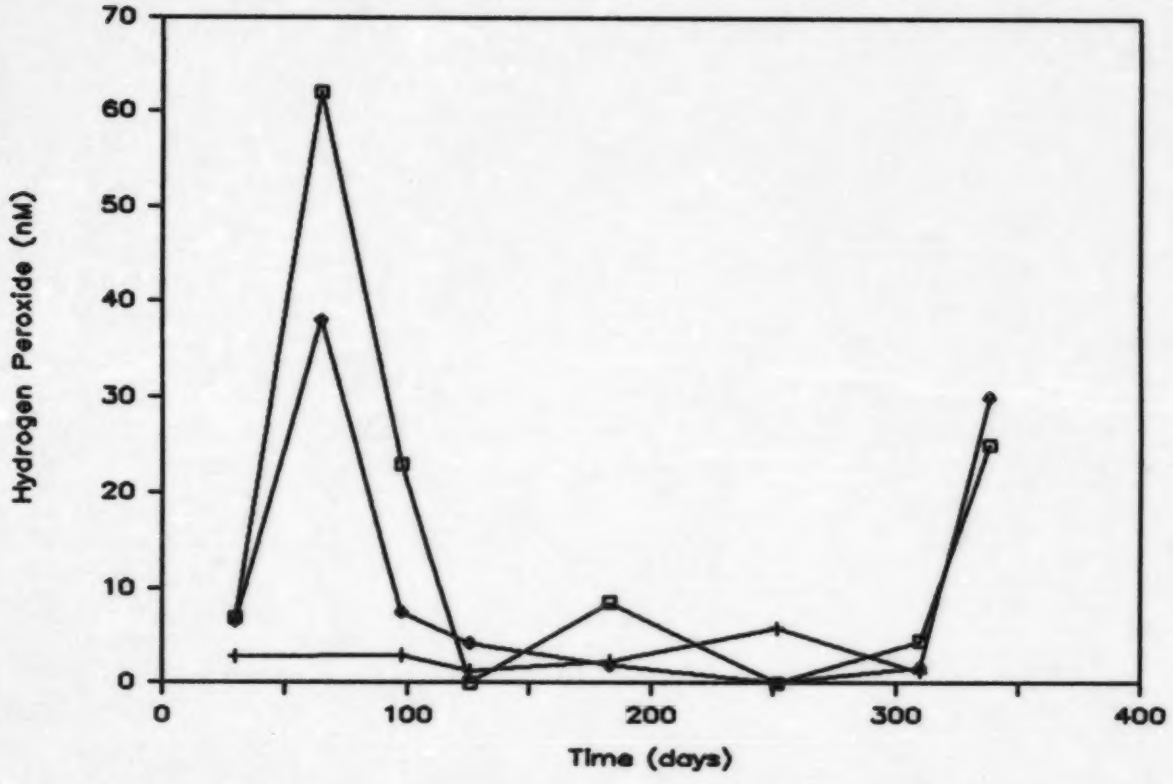

Figure 7. Time series graph of hydrogen peroxide concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

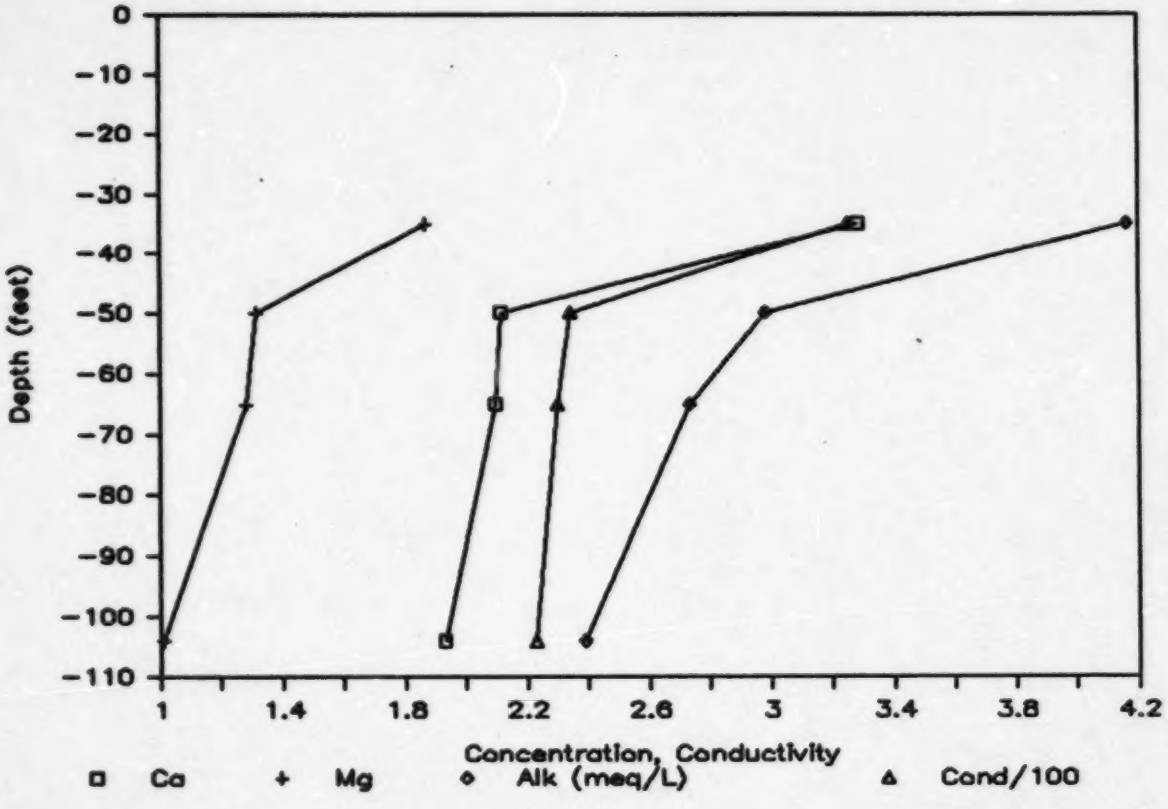

Figure 8. Concentration profiles of calcium, magnesium, alkalinity and profile of conductivities in Havana lowlands aquifer, 9/19/85. □ Ca^{2+}, + Mg^{2+}, ◇ Alkalinity, △ Specific Conductance.

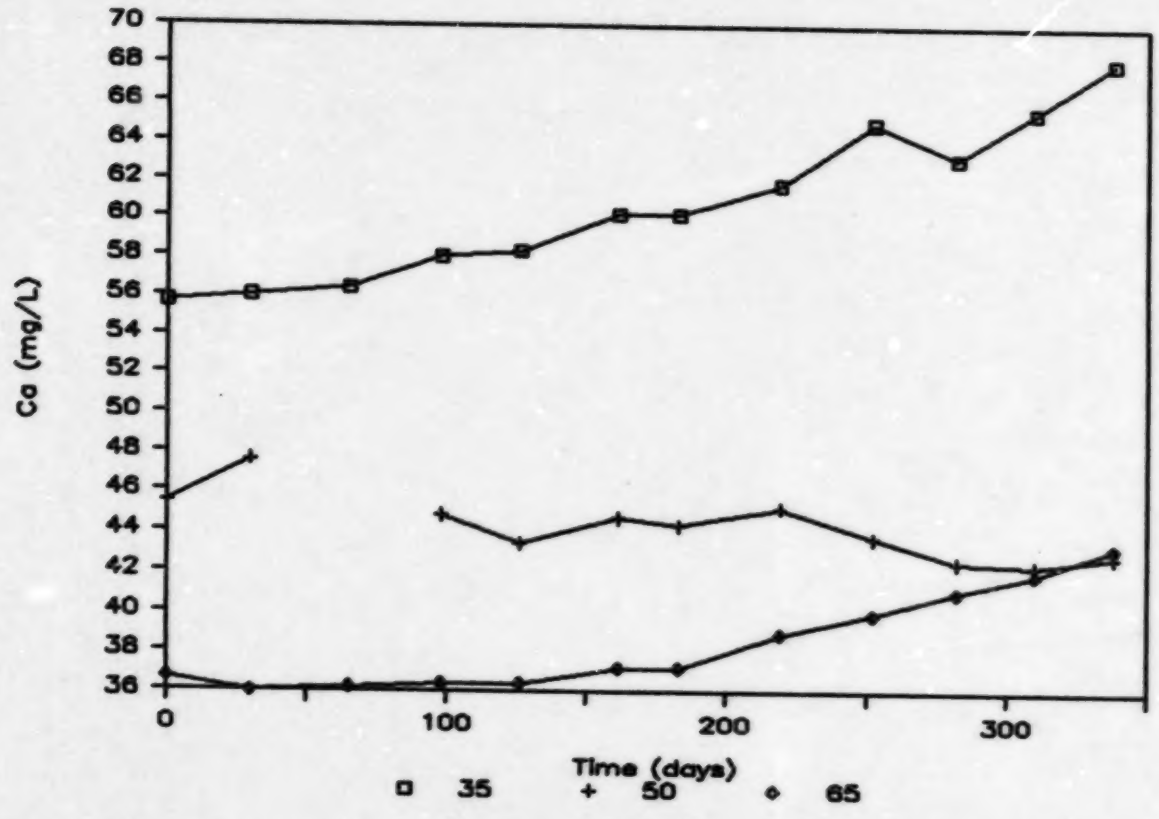

Figure 9. Time series graph of calcium concentrations in Havana lowlands aquifer. □ 35, + 50, ◇ 65 feet.

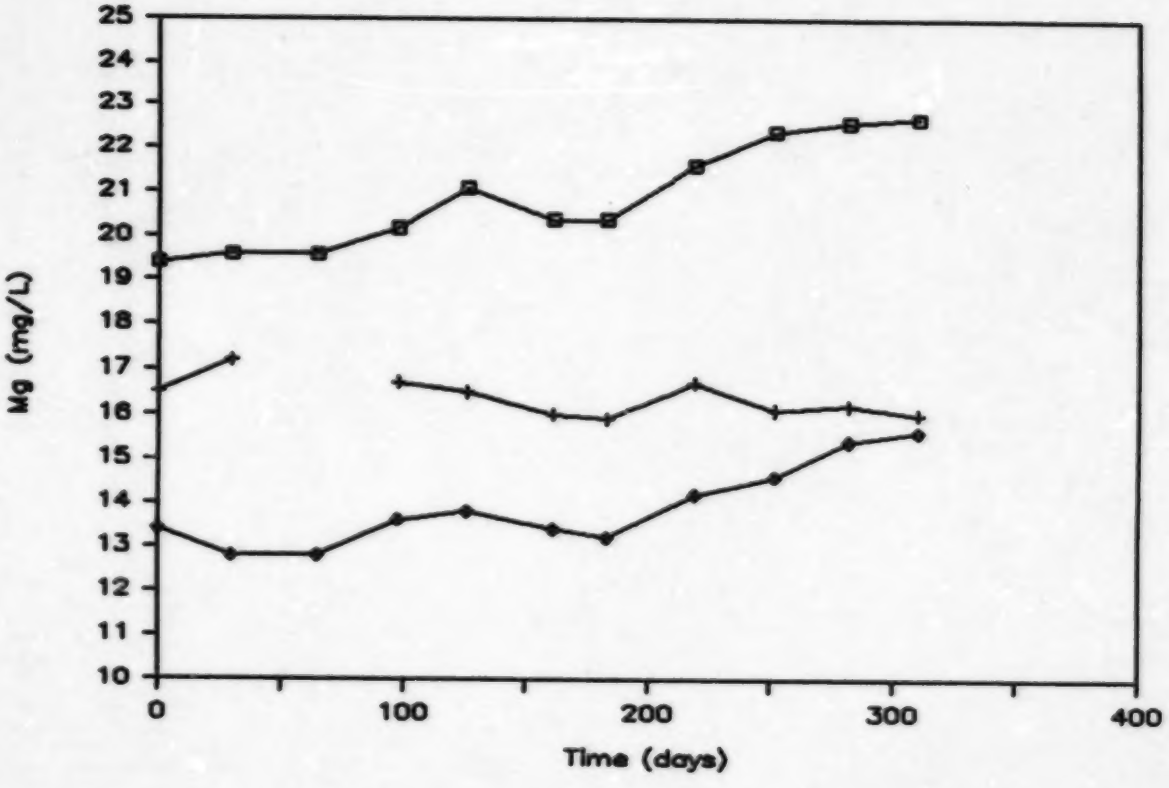

Figure 10. Time series graph of magnesium concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

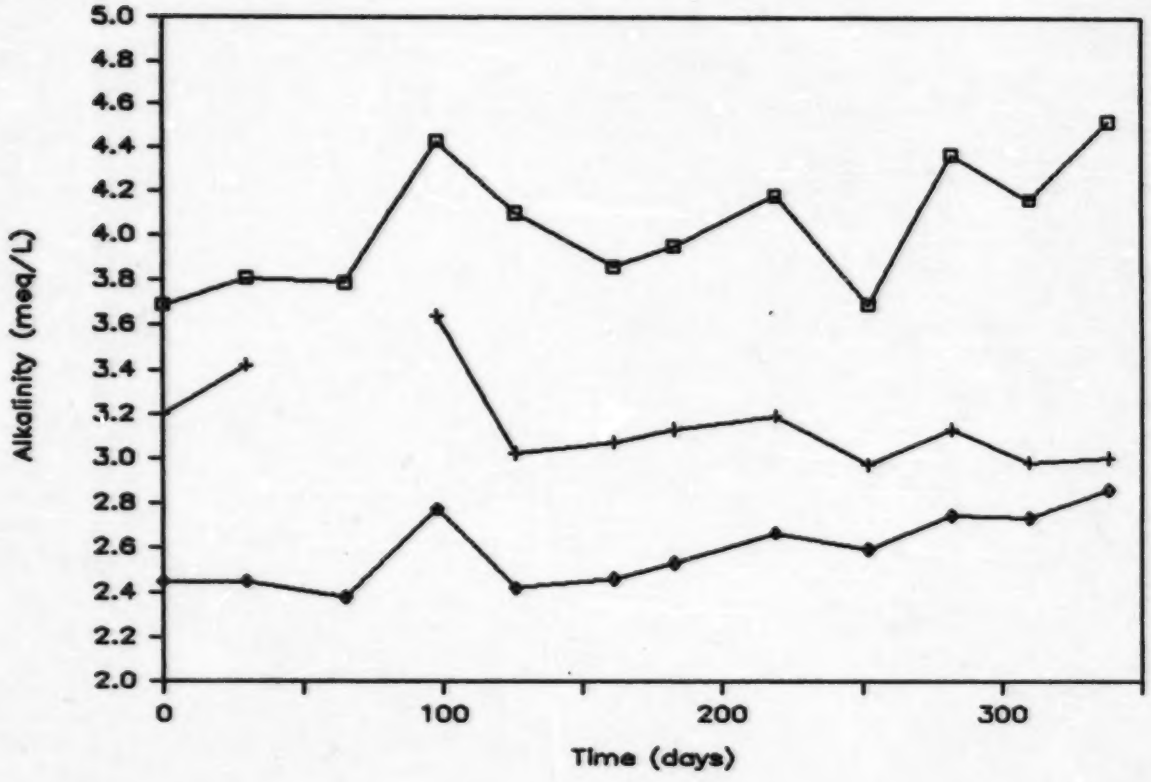

Figure 11. Time series graph of alkalinities in Havana lowlands aquifer. □ 35, + 50, ◇ 65 feet.

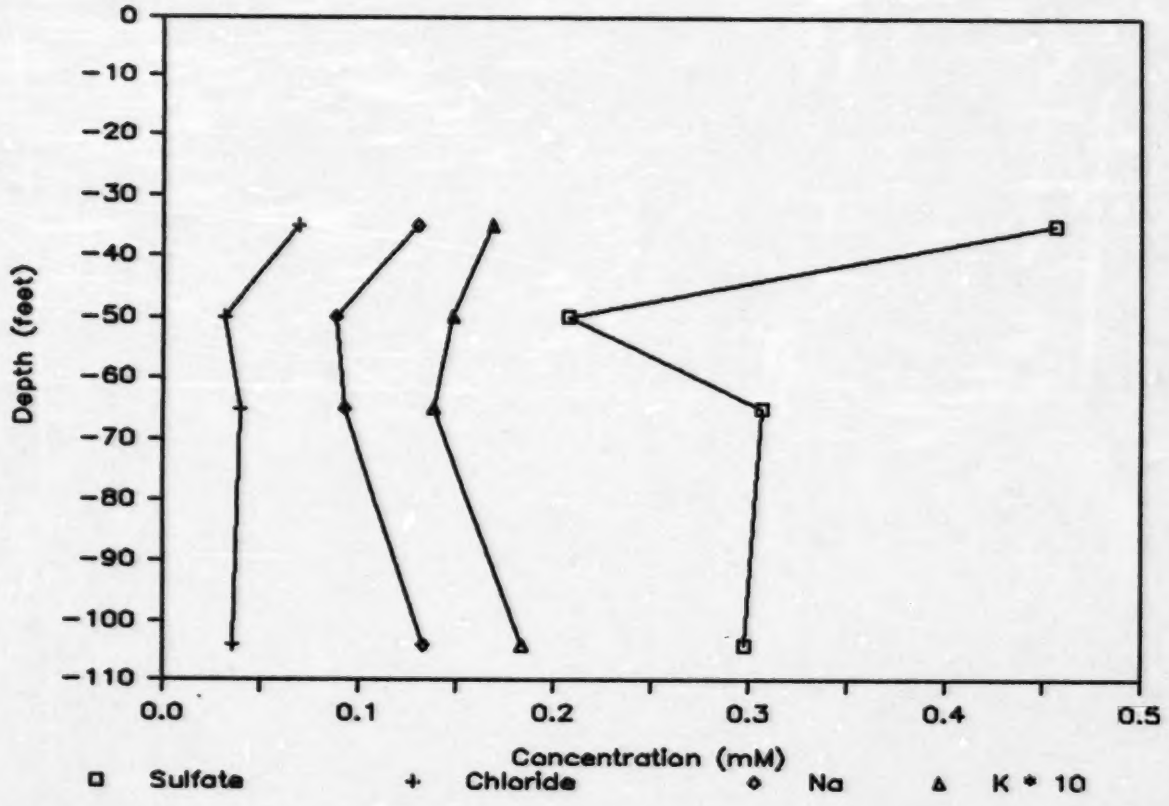

Figure 12. Concentration profiles of sulfate, chloride, sodium, and potassium in Havana lowlands aquifer, 9/19/85.
□ SO_4^{2-}, + Cl^-, ◇ Na^+, △ K^+.

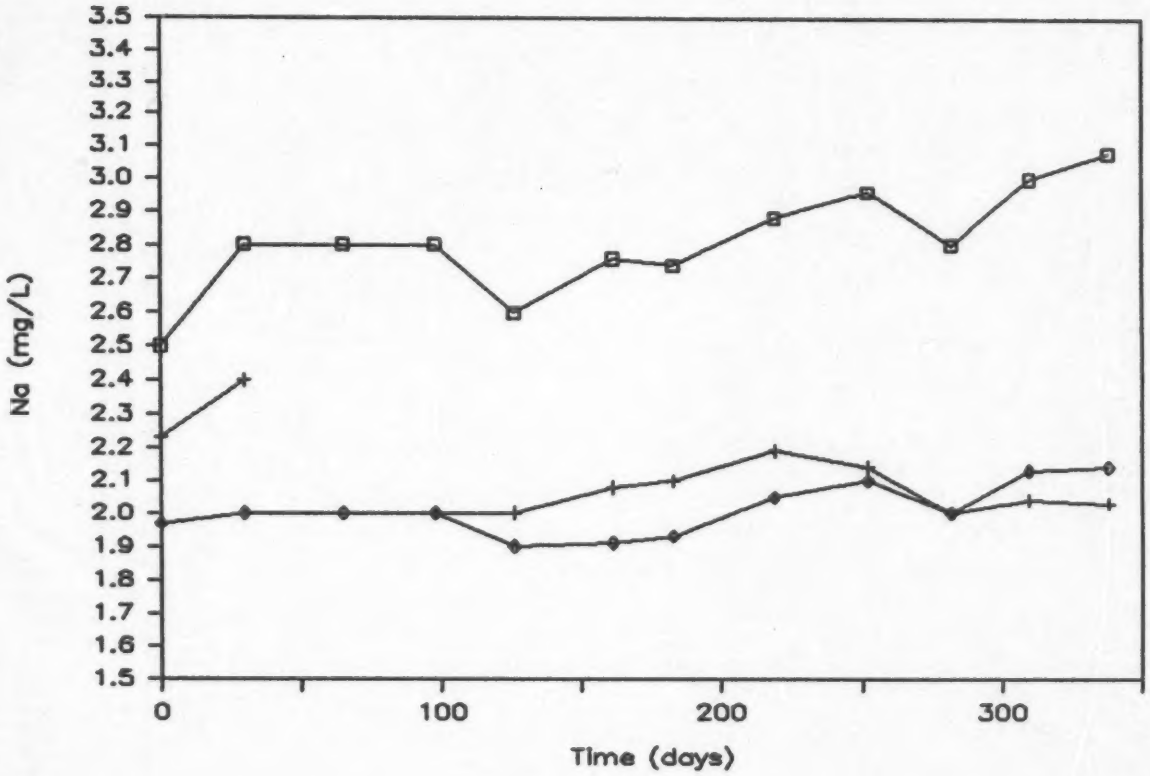

Figure 13. Time series graph of sodium concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

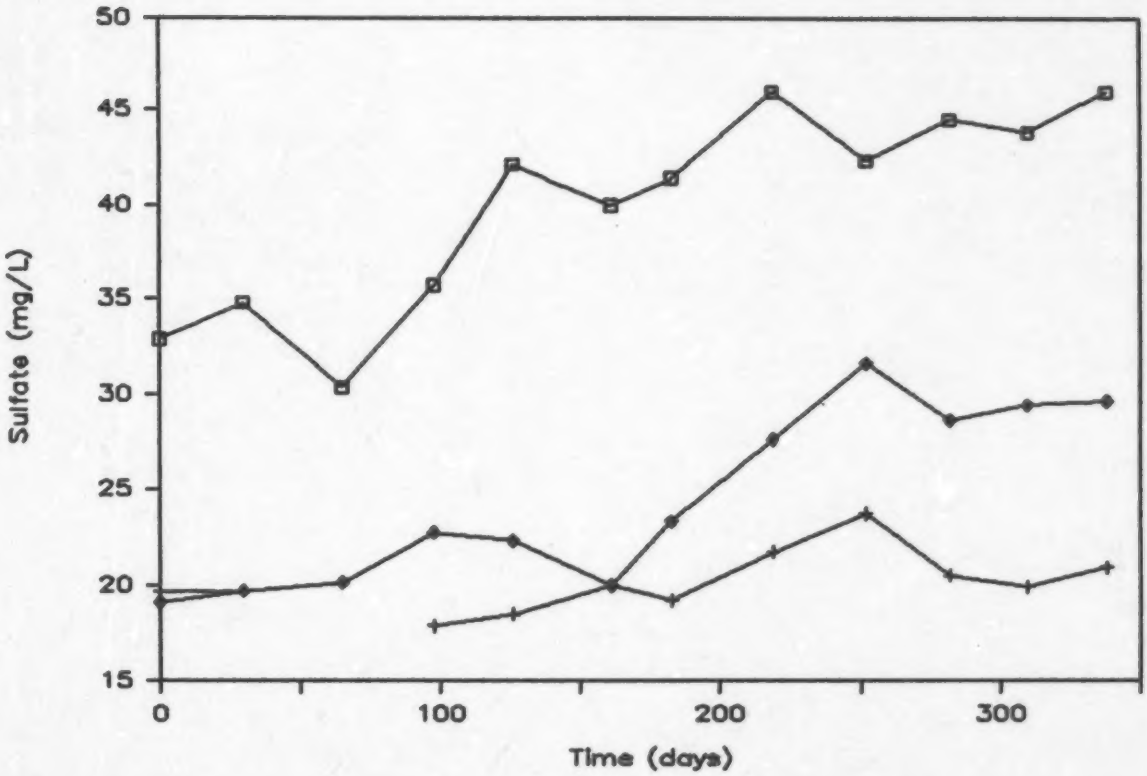

Figure 14. Time series graph of sulfate concentrations in Havana lowlands aquifer. □ 35, + 50, ◇ 65 feet.

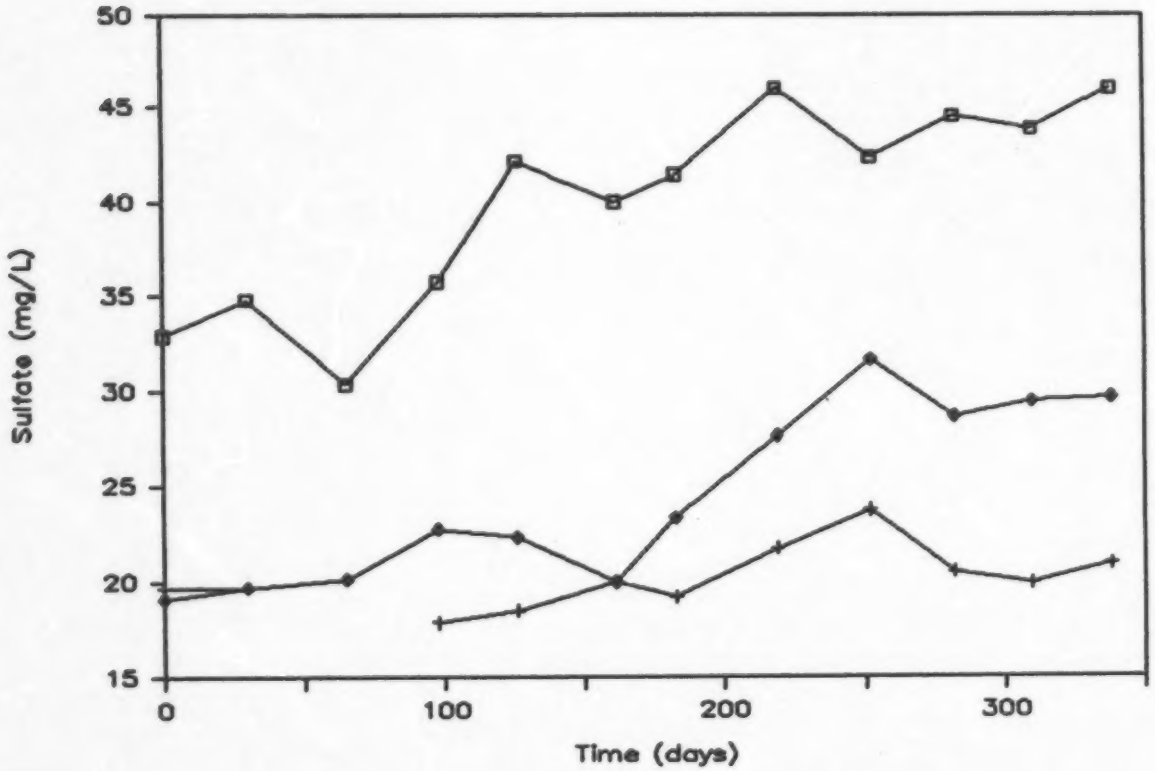

Figure 14. Time series graph of sulfate concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

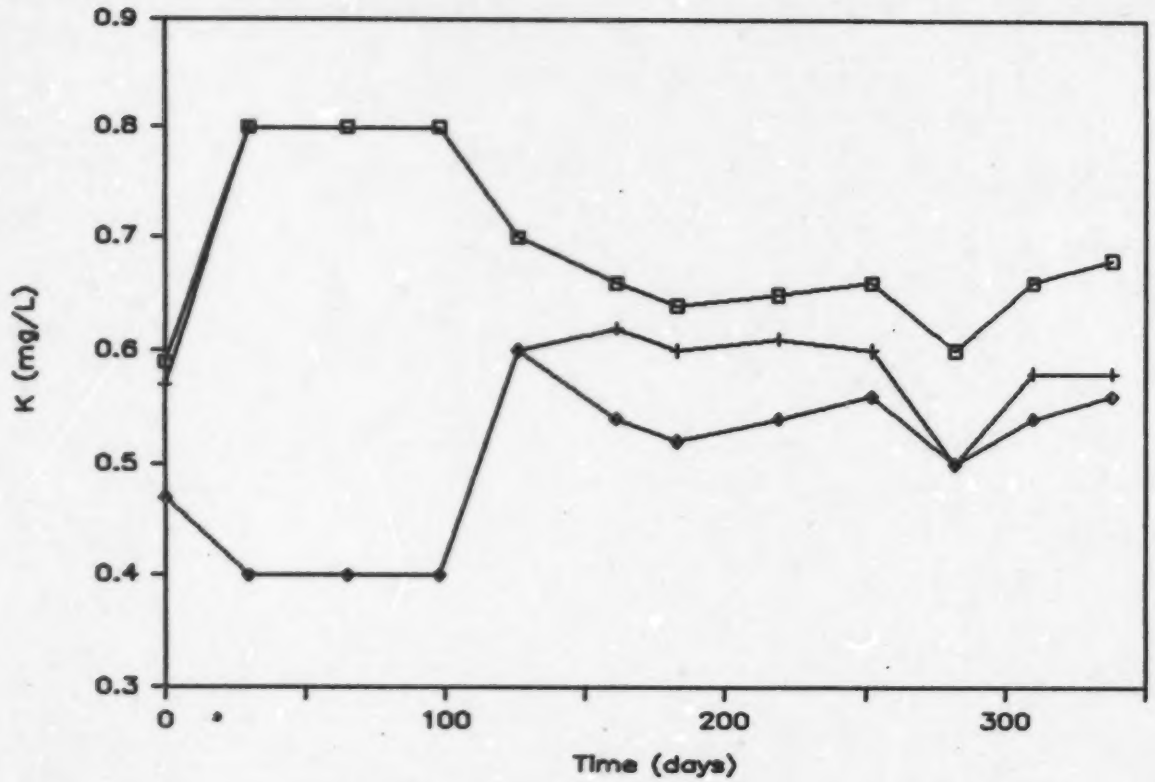

Figure 15. Time series graph of potassium concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

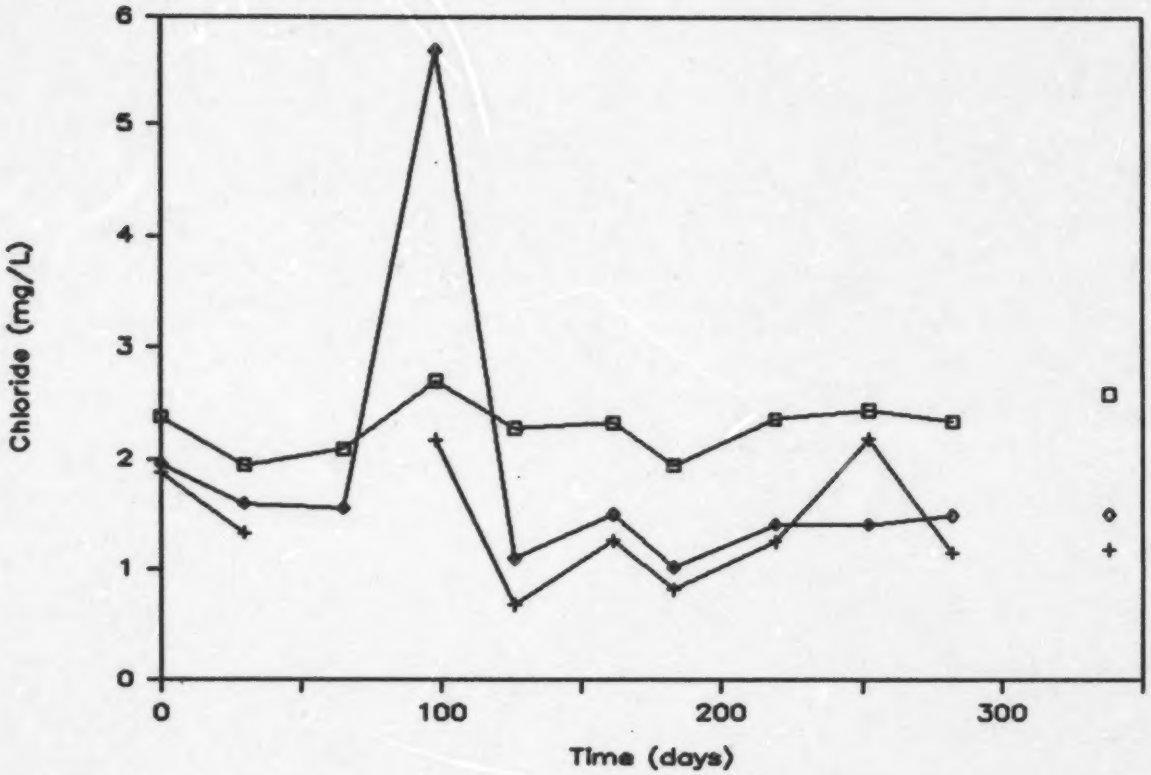

Figure 16. Time series graph of chloride concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

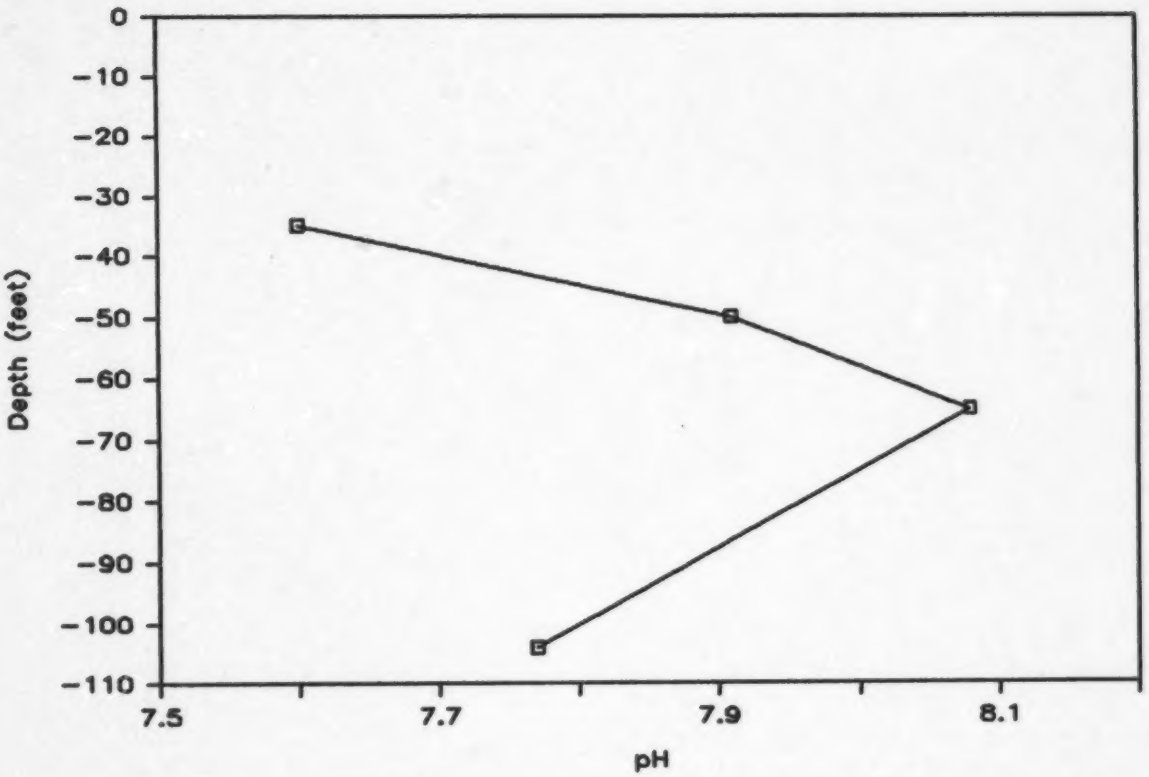

Figure 17. Profile of pH values in Havana lowlands aquifer, 9/19/85.

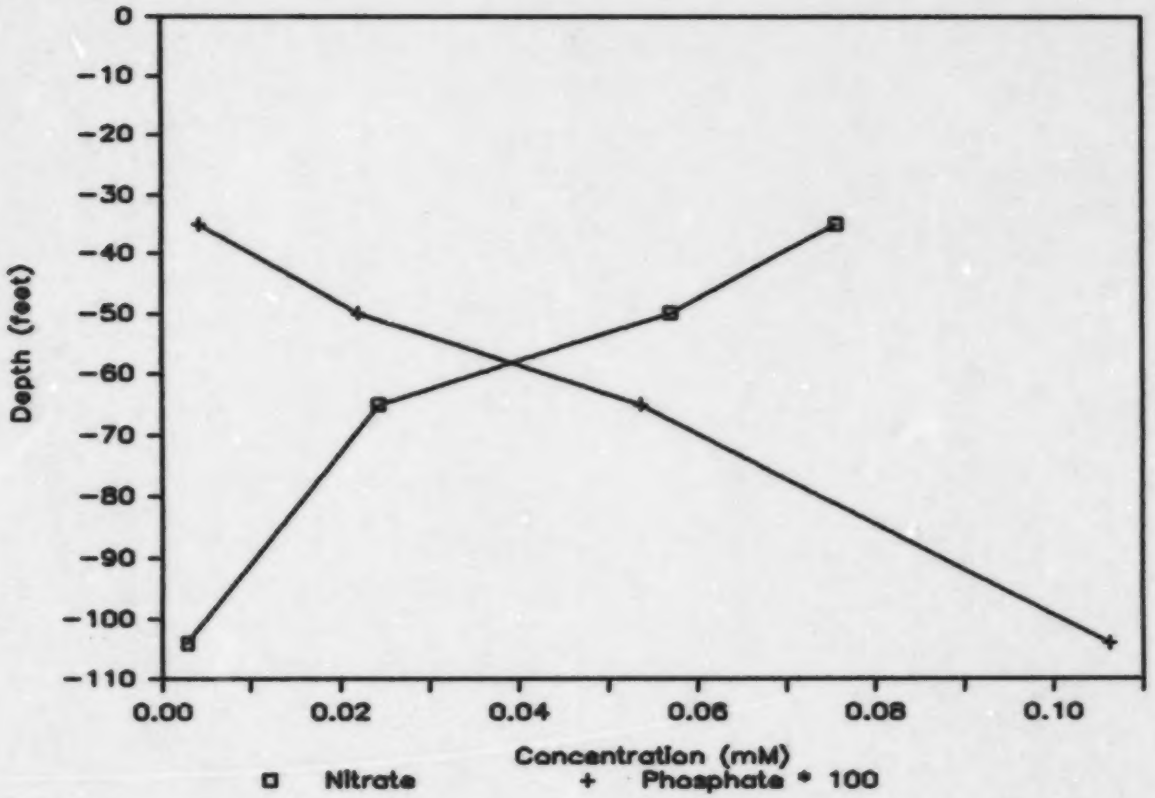

Figure 18. Concentration profiles of nitrate and orthophosphate concentrations in Havana lowlands aquifer, 9/19/85.
□ NO_3^-, + $o\text{-}PO_4^{3-}$.

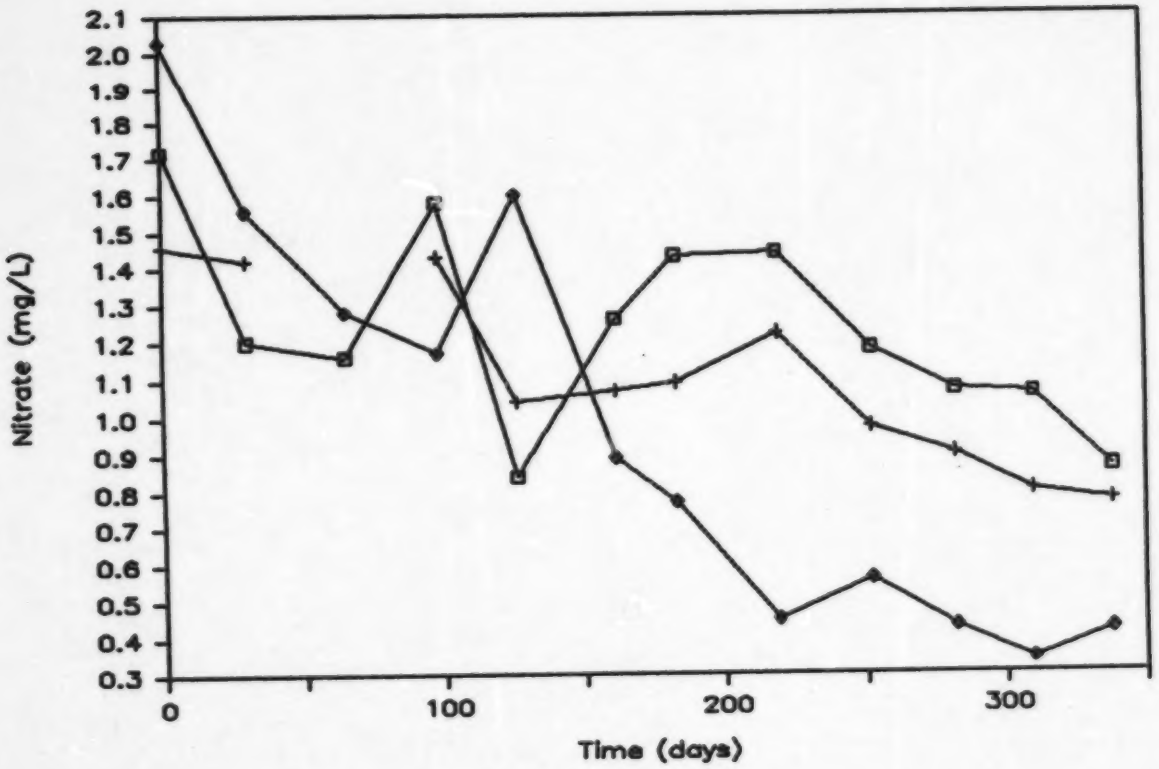

Figure 19. Time series graph of nitrate concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

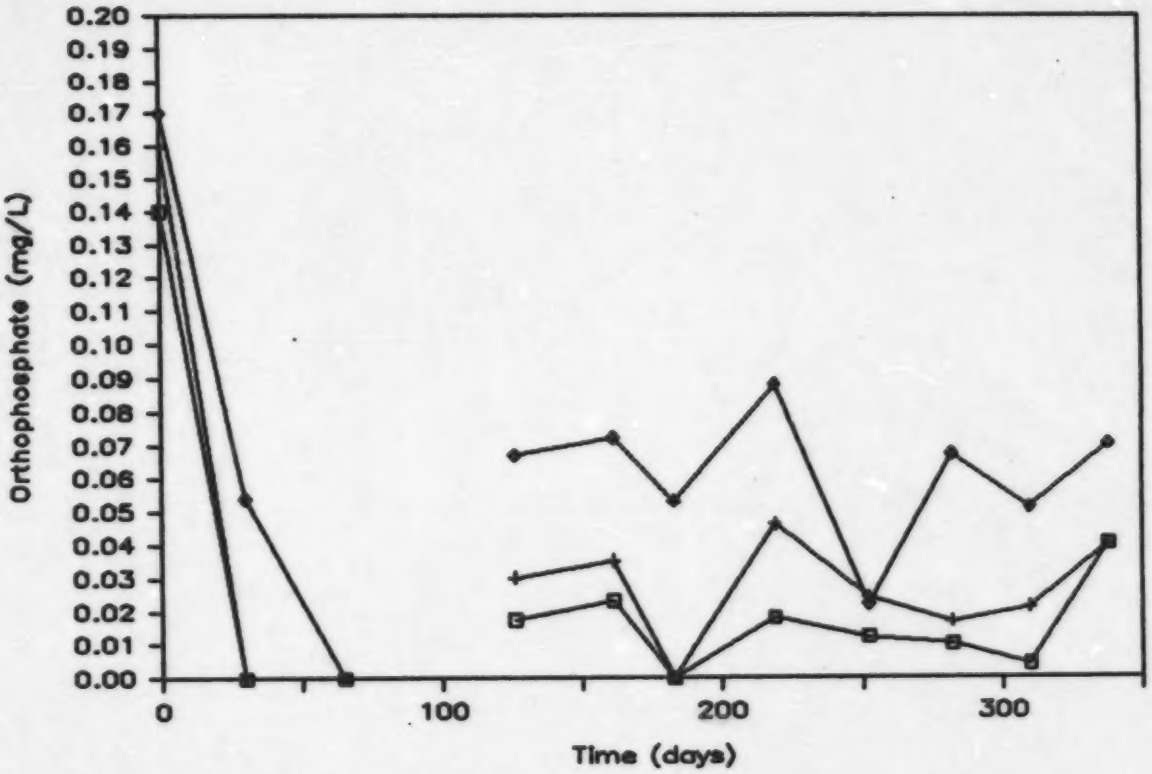

Figure 20. Time series graph of orthophosphate concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

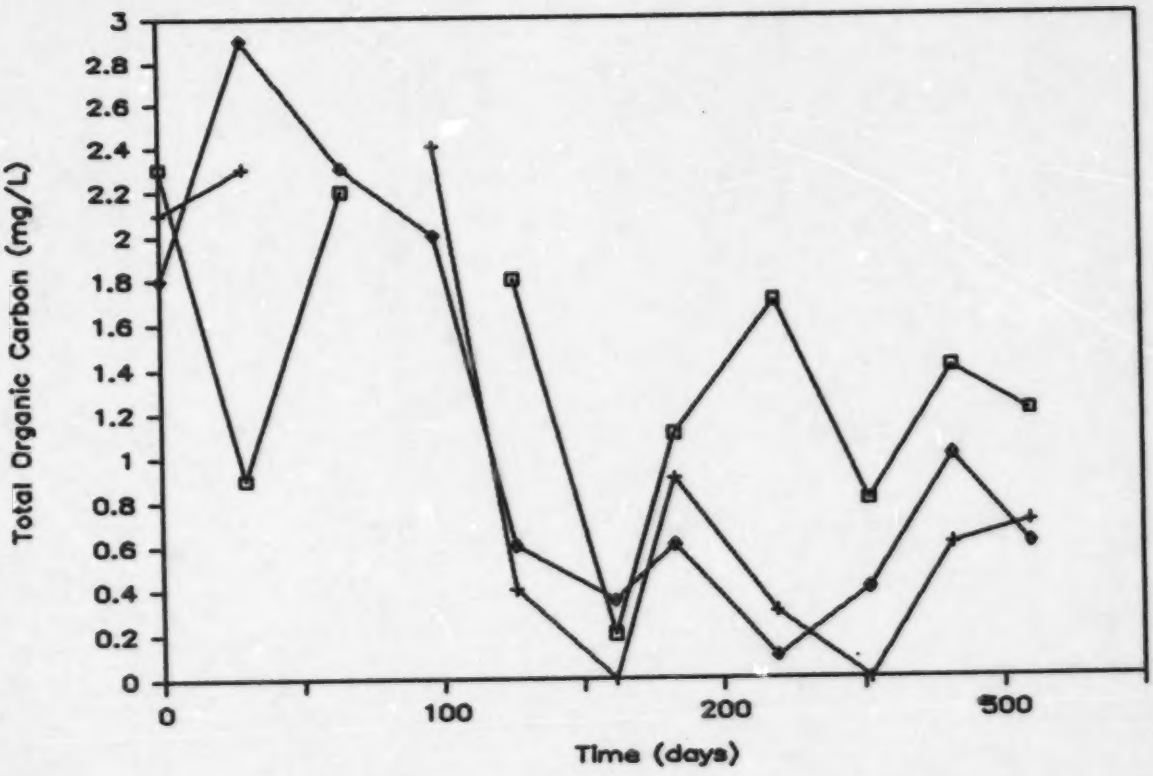

Figure 21. Time series graph of organic carbon concentrations in Havana lowlands aquifer.
□ 35, + 50, ◇ 65 feet.

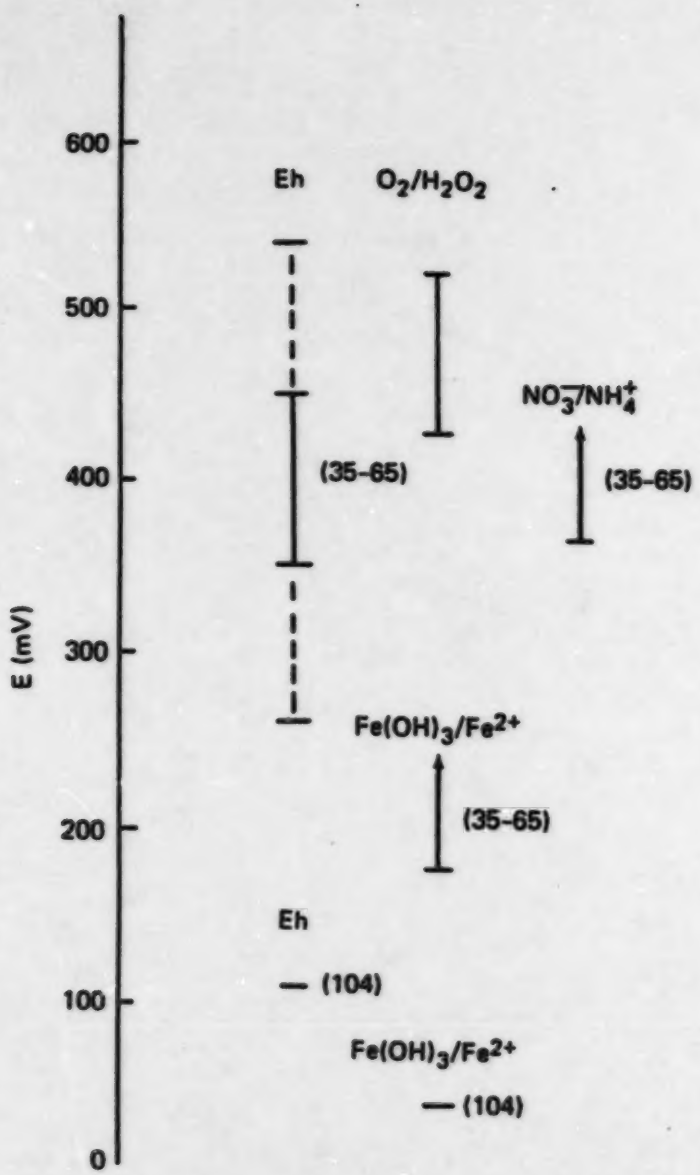

Figure 22. Comparison of measured and calculated redox potentials in Havana Lowlands ground waters.
Numbers in parentheses are depths. Dotted lines in Eh range include extreme values, solid line includes all but extreme values. Arrows indicate lower bounds of calculated potentials.